Chem Ed

EDITORIALLY SPEAKING

The problem of adequately fitting together high school and college chemistry is more than one of "correlation" or "coordination." We see the most important phase of it to be *cooperation*. Seldom have we talked with a group of conscientious high school chemistry teachers without their mentioning discouragement at having a student's established competence in chemistry ignored by college officials. They readily admit that the great majority of high school students have not had a chemical experience equivalent to that of the college freshman. But they resent—and rightfully—the assumption that no student enters college with a good grounding in chemistry.

We recall a carefully worded statement which came from the Reed Conference: (See THIS JOURNAL, **35**, 54 (1957))

> One impetus to the improvement of high school chemistry courses would be the adequate recognition of the course as the basis for future work in college. Students should be admitted to advanced standing in college chemistry as the result of examination, teacher recommendation, or course evaluation.

The kind of cooperation we applaud is typified by that described in a letter recently received from Professor Fredric C. Schmidt of Indiana University. In it he describes a placement examination system typical of those in use at many colleges and universities.

> For a student to prepare himself sufficiently well and to proceed to more advanced chemistry courses in college, he will of course need to have access to adequate laboratory facilities and good illustrative material. But most important is an awareness of the content of a general chemistry course. Both students and teachers in high school chemistry must know of the scope of the subject matter involved and the scientific philosophy which are essential in the understanding of more advanced courses. We wish to make a plea for closer cooperation between the high schools and the colleges and universities in defining the nature of this subject matter. Then perhaps more of the able students can be prepared to begin their college chemistry careers with some of the preliminary study completed and ready to go on to advanced studies.
>
> Some indication of the possibilities for precollege training has been obtained from the results of chemistry exemption examinations offered by the Indiana University Chemistry Department each year to incoming students who have studied chemistry in secondary schools. These examinations are equivalent to the final examination given for the general chemistry course at the University—the course which is prerequisite for more advanced chemistry courses in the curriculum for chemistry majors and premedical students.
>
> Of the students taking the exemption examination in 1958 there were several who felt confident that with a little more effort in the proper channels of beginning chemistry they would have been able to do much better. If the students in the borderline area had prepared for this examination with their teacher of high school chemistry, and if they and their teacher had been informed of the scope of the material given in the first semester of most general chemistry course, they would perhaps have been able to achieve grades which would definitely give them advanced rating.
>
> The subsequent records of those students who majored in chemistry after having been excused from the elementary general chemistry course have without exception been very good. Their success in advanced work fully justifies confidence in acknowledging their good high school training.

No one will argue that a simple attack can yield a simple solution to a complex problem. Nevertheless, the problem is bound to appear less complex when all involved are better informed. Certainly those who can make best use of more information are high school teachers who have highly gifted students in their classes. The success of the courses in the Admission for Advanced Standing Program of the CEEB is another demonstration that good students taught by good teachers using good textbooks can save valuable time in preparing for a career in chemistry. Even where the establishment of such courses is impractical, gifted students deserve the opportunity of preparing themselves for advanced work in college.

We hope that the many colleges and universities who identify and reward superior high school preparation are at the same time making a similar effort to improve the content of the high school chemistry course.

Professor Schmidt and his colleagues do more than talk about the problem. They put their case on the desk of every high school chemistry teacher in the state of Indiana. The information they supply includes both an outline of the present first semester chemistry course at the university and copies of a typical exemption examination. We urge readers interested in the details of this plan to communicate with the chemistry department at Bloomington.

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Three Centuries of Rochelle Salt

Rochelle salt is at present widely known throughout the world and is made on a large scale both here and abroad. As the name implies, it was first obtained (around 1660) in the French seaport of La Rochelle, near the mouth of the Gironde. The early manufacture of the salt and its sale in France and elsewhere is curiously connected with the political, economic, and religious fortunes of La Rochelle, a city that played an important part in European history in the sixteenth and seventeenth centuries. In the times of the Reformation, it became one of the chief centers of Calvinism in France. Early in the seventeenth century it was a stronghold of the Huguenot party, and in 1628 it was subjected to a siege by an army of 30,000 under the over-all command of Cardinal Richelieu, prime minister of Louis XIII. Although heroically defended, under the leadership of Mayor Guyton, the city was forced to surrender after nine months of indescribable suffering and Guyton was banished for life from his native city. The catholic religion was re-established and no protestants, except those who were citizens, were allowed inside the city. Its coat of arms with the motto, "Servabor, Rectore Deo" (I shall be safe, with the help of God), is a reminder of the protestant past of La Rochelle.

Figure 1. Original paper package of Rochelle Salt as sold in France, 1655 (still in use).

Among the valiant defenders of the city in the fateful year 1628 was the pharmacist Jehan Seignette (1592–1648), the son of a well-to-do merchant. As was the custom of many prominent citizens, Jehan Seignette also had a coat of arms which showed against a red background a white swan, swimming on the blue waves, while at the right, above a diagonal black band, appeared a red-tongued wolf's head and below a red rose. The latter, being the floral emblem of England, probably indicated family connections with that country. The swan, emblem of serenity, very likely represented the originator of the coat of arms, while the wolf's head may well have symbolized his enemies. Moreover, the young swan (cygnet in French) was no doubt a pun on the name Seignette.

Of the seven children of Jehan Seignette and Marie-Suzanne Guillemard, there were only two, Jehan (1623–1663) and Elie (1632–1698), who were active in helping their father in the study and exploitation of plants, drugs, and chemicals. Jehan, who had studied medicine at Montpellier, prescribed the preparations put up by Seignette Sr. and his son Elie. On the father's death in 1648, Elie at the age of 16 carried on, first with the aid of his brother and, when Jehan died in 1663, alone.

"Sel Polychreste" Synthesized by the Seignettes

The discovery, or rather the first synthesis of Rochelle salt, occurred some time between 1648 and 1660, possibly around 1655 (*1*). The name under which it was sold "sel polychreste" was derived by Jehan from the Greek and denotes a salt "of many virtues." The successful introduction of this new product, which was used extensively as a mild cathartic and diuretic, aroused the envy of the master pharmacists of La Rochelle, and for many years they agitated against their lone protestant colleague who—for obvious reasons—had never applied for a certificate of master pharmacist. In spite of repeated attempts to prevent Elie from continuing his profession, he remained a manufacturing pharmacist till the end of his life. This fortunate reprieve was due in large part to the personal intervention of Louis XIV, who, in 1673, gave Elie a brevet saying:

> La dite Majesté, voulant par ces considérations gratifier et personnellement traiter ledit Seignette elle luy a permis et permet, conformémant a l'avis du sieur de Terron, de continuer dorénavant si bon luy semble, l'exercice publicque d'apothicaire à La Rochelle.

It is quite likely that the synthesis of Rochelle salt by the Seignettes resulted from the inadvertent use of

sodium carbonate instead of potassium carbonate, which they had hitherto used to make cream of tartar (acid potassium tartrate) more soluble. In his treatise on the "false" polychrest salt, Elie (*2*) states that the genuine salt is made from three kinds of salts which, when put together, produce "un remède peu composé mais pourtant trés utile, trés innocent et très facile à prendre." This would indicate the use of both carbonates together with cream of tartar to give potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$). The salt was sold at "30 sols la prise" (later reduced to 20 sols) in packages showing on the cover the swan of the family coat of arms, illuminated by the rays of a distant sun and the Latin inscription "cum sole et sale omnia fiunt" (with sun and salt all things are accomplished). A picture of a wreath (with enclosed monogram of the letters E, J, S, S, P) and the title "Le vray Polychreste de Messrs Seignette de La Rochelle" (Fig. 1) served to protect customers against imitations also sold as sel polychreste.

Most of these spurious products were nothing but potassium sulfate, obtained by calcining sulfur with potassium nitrate, often mixed with residual sulfur. This salt, also known as Glaser's salt, had been introduced into pharmacy by Christophe Glaser, demonstrator of chemistry at the Jardin du Roi in Paris.

In order to combat the sale of the false polychrest salt, Elie Seignette (Fig. 2) went to Paris in 1664, distributed samples of his salt to the sick, to physicians, and to pharmacists, and appeared in person before the "Assemblée physique," which recommended and adopted the use of Seignette's salt. Having appointed a surgeon, Rousseau, as his representative, Seignette then returned to his home town. Seven years later he came back to Paris to cope with the sale of imitations by his own representative and others. He re-appeared before the "Assemblée physique" and demonstrated with "heat" and "water" the profound difference in behavior between his salt and that of Glaser. In the same year (1672) he became acquainted with a pupil of Glaser, the young pharmacist Nicolas Léméry (1645–1715), a fellow Calvinist, who accepted samples of Rochelle salt for distribution among friends and acquaintances. In his celebrated "Cours de Chymie," first published in 1675, Léméry still calls Glaser's salt "Sal Polychrestum" and subsequently mentions the salt of Seignette in the following terms (*3*):

> Monsieur Seignette, an Apothecary of La Rochelle, hath put in Use a certain Sal Polychrestum, which seems at first to be like unto this, but when it comes to be examined, there is found a notable Difference, as well in the Chrystallizations (and when it is thrown into the Fire) as in the Effects; for whereas six Drachms of this Sort (Salt-peter, fixed by Sulphur and by Fire) do cause Gripes in pricking the Membranes of the Stomach, that of Mons. Seignette in the same Quantity, doth purge very gently without any Gripes at all, as he proves in a little Treatise that he hath made touching the Uses of this Polychrestum. And the Truth of it I have found myself in several Persons. The Composition of this Salt is known to none but himself, who having given it a Reputation in the chiefest Towns of France, has left some Quantity of it with me to distribute, and make Use of here at Paris. Several Persons have endeavoured to counterfeit this Salt, but failed of Success. M. Seignette, Physician to his Royal Highness, the Duke of Orleans, who lives now at La Rochelle, continues to prepare and send the same to me.

On account of his religion Léméry was forced to leave Paris in 1683, and he did not return until 1686, when he

Figure 2. (Bibliotheque Nationale, Paris Service photographique).

became a catholic to save himself from persecution. His friend Seignette, on the other hand, remained faithful to the doctrine of Calvin till the end of his life. He died on May 2, 1698, and was survived by his wife Elizabeth Perdriau (whom he had married on January 24, 1654) and 10 children. Two of these, his namesake Elie (1657–1736), a drug merchant, and Pierre (1660–1719), a physician, continued the manufacture of the genuine polychrest salt. It is this son Pierre who is often (*4*), erroneously, credited with being the Seignette who first made the salt in 1672. He was then only 12 years old. This error is probably due to the fact that Elie had a brother Pierre, a merchant through whose efforts the salt was introduced in England and in the "American Islands" (i.e., Montreal and the surrounding countryside). This very likely explains why Rochelle salt is already mentioned in the *London Pharmacopoeia* of 1788 under the name of Natron Tartarizatum and 32 years later in the first edition of the *Pharmacopoeia of the United States* as Tartrate of Potass. and Soda, called "Rochelle Salt."

The secret of the manufacture of Rochelle salt was maintained for well over 70 years, and it was not until 1731, that the problem of its composition was solved independently by two pharmacists in Paris, Simon Boulduc and Claude Joseph Geoffroy. The former published his data in the Mémoires de l'Académie des Sciences for 1731 (p. 124) while Geoffroy communicated his discovery to Sir Hans Sloane, President of the Royal Society, who publis'ed it in the

The Cover

Rochelle salt single crystal bars and oriented piezoelectric elements cut from these.

Courtesy of Clevite Corporation

Philosophical Transactions for that year. Rochelle salt, or "Seignette salt," retained its reputation as a household remedy for gastric disturbances until well into the twentieth century. It is still used as a constituent of Seidlitz powders, which consist of free tartaric acid kept in a blue package and a mixture of sodium bicarbonate and Rochelle salt in a white package. The contents of each package are dissolved separately in water and then both solutions mixed.

The use of Rochelle salt for purely chemical purposes goes back to 1858 when Fehling (*5*) replaced neutral potassium tartrate by the more easily crystallizable Rochelle salt which as he said "is readily obtained pure commercially." He used the salt in his well-known Fehling's solution for the quantitative determination of sugar. The salt is also used as a reducing agent for obtaining silver mirrors on glass as was first suggested by Liebig in his efforts to eliminate (poisonous) mercury mirrors from household articles.

Pyroelectric Properties

Among the physical properties of Rochelle salt that have been most frequently studied by crystallographers and physicists are those dealing with its pyroelectric and its piezoelectric behavior. That Rochelle salt is pyroelectric was discovered in 1818 by Sir David Brewster (1781–1868) (Fig. 3) and was described by him in 1824 (*6*). Pyroelectricity had been known in Europe since 1703 when crystals of tourmaline were shipped from Ceylon to Holland. The sailors used to amuse themselves by putting the crystals into the hot ashes of their peat fires, when the pyroelectric effect became manifest by the ashes gathering at one end of the crystal. For this reason tourmaline became known in Holland as *asch-trekker* (ash-attractor). Brewster (*loc. cit.*, p. 208) states that the first discoverer is unknown and adds that pyroelectricity was first mentioned by Léméry in 1719. In the next hundred years it was studied by Aepinus, Wilson, Canton, Priestley, and finally by the noted French crystallographer, the Abbé René-Just Haüy (1743–1822) who added several minerals to the list of pyroelectric substances. Brewster was the first scientist who discovered the pyroelectricity of crystals grown from aqueous solutions. Of the 14 substances he investigated (Rochelle salt, tartaric acid, ammonium oxalate, the chlorides of potassium and mercury, the sulfates of magnesium, ammonium, iron and magnesium-sodium, potassium cyanide, potassium carbonate, lead acetate sugar, and citric acid) he found that the tartrate of potash and soda (Rochelle salt) and tartaric acid were "pyroelectric in a very considerable degree," but the action of several of the other salts was comparatively feeble.

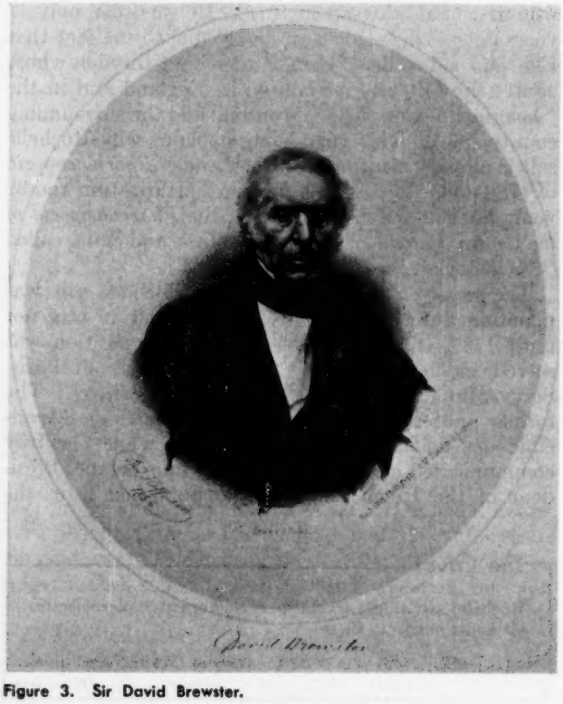
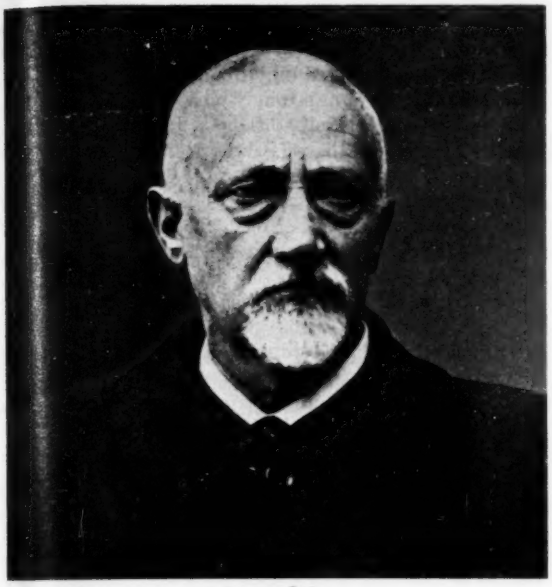


Figure 3. Sir David Brewster.

In studying pyroelectricity in crystals, frequent use is made of a method, first proposed by Kundt (*7*), which consists of dusting the uniformly heated crystal with a mixture of powdered sulfur and red lead. The positive end of the crystal (called the analogous) becomes red and the negative end (the antilogous) yellow. This method has been successfully applied to Rochelle salt by H. Müller of MIT. He found that only in a narrow range of temperatures (about 40 degrees) does the salt show pyroelectric properties. Although several minerals and salts are pyroelectric, their number compared to those that are piezoelectric is fairly small. A study of the 32 possible classes of symmetry in which crystals can be divided reveals that there are 21 that lack a center of symmetry. Of these, 20 are piezoelectric, i.e., crystals belonging to these 20 classes *become* polarized when an external stress is applied. Of the 20 piezoelectric classes only 10 exhibit a pyroelectric effect which means that they are *spontaneously* polarized; however, the polarity is generally masked by surface charges, but becomes evident on heating the crystal (hence the name *pyro*-electricity). It can, therefore, be said that all pyroelectric crystals are also piezoelectric, but the converse is not necessarily true. No practical applications of pyroelectricity have been reported. In crystallography it has been used to identify certain classes of symmetry.

Piezoelectric Properties

Of much greater significance, on account of its many technical applications, is the piezoelectric effect in Rochelle salt. Cady in his monumental work on this topic (*8*) devotes about 150 pages out of a total of 750 to Rochelle salt, while the related topic of pyroelectricity takes up only one chapter of 12 pages. Piezoelectricity was discovered in 1880 by Jacques Curie (1855–1941) and his better known younger brother Pierre Curie (1859–1906) (Figs. 4 and 5). It is interesting to note that both started their scientific career, like their compatriot Pasteur 30 years earlier, with the study of crystals and that they, like Pasteur, included Rochelle salt in their studies. Knowing that there exists a certain relation between crystal structure and pyroelectric behavior, which implies the existence of one or more polar axes, they applied pressure, *not at random*, as had been done already, first by Haüy and later by A. C. Becquerel, but *in the direction of the so-called*



Jacques Curie

Figure 4.

hemihedral axes of several pyroelectric crystals (zinc blende, sodium chlorate, boracite, tourmaline, quartz, calamine, topaz, tartaric acid, cane sugar, and Rochelle salt). Putting a properly cut crystal plate, provided with tin-foil electrodes, under pressure, they produced a charge, measured with an electrometer, that was proportional to the applied pressure. This is the *direct,* or generator effect of piezoelectricity. The converse effect, which deals with the motor property of piezoelectric crystals, consists in the deformation of the crystal that is directly proportional to the applied electric field. This effect was predicted by Lippmann in 1881 and was verified experimentally in the same year by the Curies.

Further progress in general knowledge of piezoelectric crystals was made by Lord Kelvin in Britain and by F. Pockels and W. Voigt in Germany but it was only toward the end of the first world war, in 1917, that Rochelle salt, on account of its unusually high piezoelectric effect, became a widely used object of investigation in acoustics and electronics. In that year Nicolson, at Bell Telephone Laboratories, constructed loudspeakers, microphones, and phonograph pickups with crystals of Rochelle salt. The next year Cady, in some of his early work on high-frequency resonators and oscillators, used Rochelle salt crystals as frequency regulators (*loc. cit.*, p. 287). He soon found, however, that quartz, on account of its superior mechanical and thermal properties was to be preferred to Rochelle salt for this purpose. The same year (1918) Cady and, independently, Anderson studied Rochelle salt for its possible use in submarine detection and discovered an anomalous electric effect in the salt, closely connected with its piezoelectric behavior. Three years later Valasek (*9*) made a thorough investigation of the anomalies discovered by Cady and Anderson.

Spontaneous Polarization

The electric displacement (as measured by the charge on a condenser) in the direction of the X-axis of the crystal, is not uniquely determined by the applied electric field, but depends also, as Valasek discovered, on its previous values. If the field is first increased to a maximum and then decreased through zero to a maximum in the opposite sense, the curve of the displacement assumes the shape of the well-known ferromagnetic hysteresis loop in iron. This can only mean that the crystal is spontaneously polarized, i.e., it has a polarization which remains when the applied field is zero and a definite coercive field is required to reverse the polarization of the crystal. The analogy with iron goes even further: just as in iron the ferromagnetism disappears at the Curie point, Valasek showed that the hysteresis loop of Rochelle salt shrinks with a rise in temperature and merges into a line at 24°C. Valasek called this point, therefore, the Curie point, or rather the *upper* Curie point, because on cooling the salt below 0°C there is another temperature (−18°C) at which the spontaneous polarization of the crystal again disappears. This behavior is without parallel in ferromagnetism. In fact, Rochelle salt is unique, thus far, in having both an upper and a lower Curie point. Other piezoelectric substances have subsequently been found to have only one Curie point. This peculiar electric behavior is designated in this country as ferroelectricity, a name first proposed by H. Müller in 1935. The term "Seignette electricity," first used by

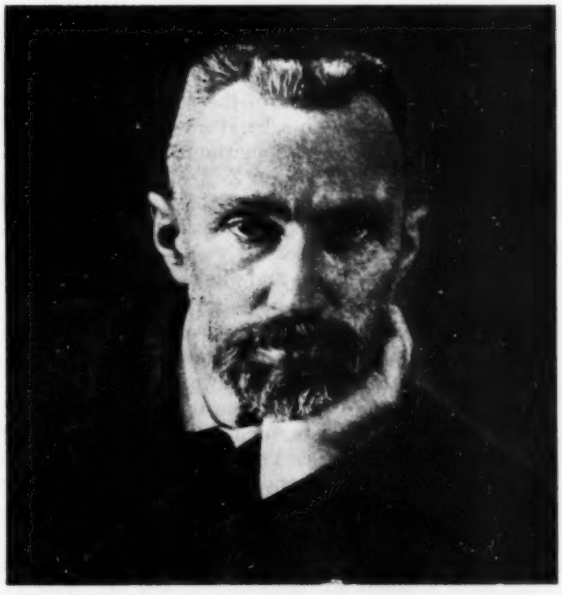


Figure 5. Pierre Curie

Kurchatov in 1933 is in common use abroad but is not popular in English speaking countries for the reason that "ferroelectric is euphonious while Seignette electricity grates on the ear" (*10*).

The fact that Rochelle salt exhibits spontaneous polarization only along its X-axis, makes this axis polar. This conflicts with the statement that Rochelle salt crystals are orthorhombic with 3 two-fold axes of symmetry. That both statements are true and do not conflict, became evident in 1937 when Jaffe (*11*) discovered that the salt is monoclinic at temperatures

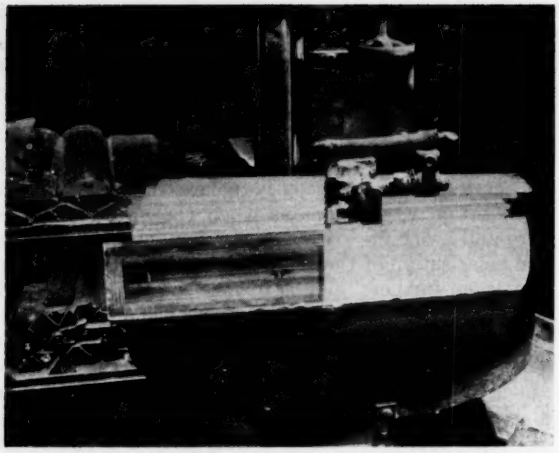


Figure 6. Rochelle salt crystals being sliced perpendicular to their ferroelectric axis. (Courtesy of Clevite Corporation.)

between +24°C and −18°C. Above 24° and below −18° it is rhombic. It is evident that only the monoclinic crystals are ferroelectric.

With regard to the piezoelectric uses to which Rochelle salt has been put, it must be emphasized that a prime requirement is the production of large, perfect crystals. In this country the Clevite Corporation, as the successor of the Brush Development Company of Cleveland (Ohio), is pre-eminent as grower of excellent Rochelle salt crystals. It is also clear that crystals are preferably cut in plates, bars, or strips at right angles to the X-axis, i.e., parallel to the Y-Z plane (Fig. 6). The cutting is done with a band saw or a wet string. The effect of distortion in longitudinal strips (cut at a 45-degree angle to the Y- and Z-axes) can be, and frequently is, magnified by the use of two strips glued together, one expanding, the other contracting over its whole length. These so-called "bimorphs" are available in a variety of shapes and dimensions.

In spite of their many desirable characteristics, Rochelle salt crystals can be used only over a limited range of temperature. They decompose at 55°C and, unless suitably shielded by a wax coating, may lose water and dehydrate. Mechanically, their strength is rather limited. These are some of the disadvantages of this otherwise highly useful salt, which have led to the search for other ferroelectric substances. It has been estimated that at present well over a thousand piezoelectric substances have been examined, of which about 100 have been thoroughly investigated. Of these not more than a dozen are used in practical applications. At the start of the second world war, Rochelle salt crystals were widely used for transducers in underwater signaling. Before long they began to be displaced by crystals of ammonium dihydrogen phosphate (ADP), which, although not as strongly piezoelectric as Rochelle salt, possesses other advantages. In the phonograph field, polarized ceramic barium titanate is competing with Rochelle salt.

The widespread activity in the scientific study of Rochelle salt dates back to 1930 and the number of papers that have been written on this salt in this country and abroad runs in the hundreds. Articles published till early in the forties have been summarized in Cady's book in 1946. Since 1945, technical and scientific interest has shifted more and more to the newer ferroelectrics. In recent years, however, there has been a revival of interest in Rochelle salt, both in Russia and in Japan, and we may confidently look for many more data regarding the properties of this remarkable salt.

While the foregoing brief sketch of the diverse uses of Rochelle salt is necessarily incomplete, sufficient data have been presented to give an idea of the versatile nature of the salt which fully justified its original designation as "polychrest salt," a salt "of many virtues."

Acknowledgment

For valuable information received, the author is indebted to Drs. Barzun, Cady, Huntington, Jaffe, Mason, and Ross, and in particular to Mons. A. Léveillé, Director of the Palais de la Découverte in Paris, and Mlle. de Saint-Affrique, librarian of La Rochelle, who furnished the data on the early history of Rochelle Salt.

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Chem Gems—Metallo–Organic Possibilities

Metals

Parallels

A Chem Ed SYMPOSIUM

Kekulé–Couper Centennial

Introduction[1]

Within one month in 1858 two papers appeared that were to have decisive influence on the development of theoretical organic chemistry. August Kekulé's article was entitled "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon" and contained the passage:

> I regard it as necessary and in the present state of chemical knowledge, as in many cases possible, to explain the properties of chemical compounds by going back to the elements themselves.[2]

Couper's "On a New Chemical Theory" began:

> I go back to the elements themselves of which I study the mutual affinities.[3]

Each then repeated the axiom of the tetravalence of carbon already in the literature and propounded for the first time the concept of chain formation of carbon atoms. These two principles represent the cornerstone of the structural theory.

Hundredth Anniversary Commemorated

The hundredth anniversary of the structural theory was commemorated in Chicago, London, Ghent, and Heidelberg.

Chicago. A Centennial Symposium on the Development of Theoretical Organic Chemistry was held as part of the fall meeting of the American Chemical Society. Further, Herbert C. Brown delivered the Kekulé-Couper Centennial Lecture.[4] The symposium papers published in this issue of the JOURNAL deal first with Kekulé's experimental work prior to 1858 and its bearing on Kekulé's theoretical views (by E. Hiebert). This is followed by a careful analysis by H. Leicester of the contrasting claims made in recent years as to the relative significance of Kekulé and Butlerov. The final three papers deal with developments in theoretical organic chemistry necessitated by the discovery of phenomena not explained by the original structural theory. On the one hand there were discovered certain instances where several compounds corresponded to the same structural formula. The philosophical problems underlying the present conception of "optical isomerism" are developed by J. Senior, while the field of geometrical isomerism is dealt with in the first half of the Ihde paper. On the other hand are instances where a substance seemed to correspond more or less exactly to several structural formulas. Tautomeric phenomena are discussed in the latter part of Ihde's paper, while the early history of the resonance concept is developed by E. Campaigne.[5]

London. Under the auspices of the Organic Chemistry Section of the International Union of Pure and Applied Chemistry, the Chemical Society (London) organized "The Kekulé Symposium on Theoretical Organic Chemistry." It was held September 15–17, 1958, and consisted of 18 papers on current theoretical problems by some of the leading chemists of Western Europe and America. The symposium was preceded by a booklet of abstracts published by the Chemical Society which also included an excellent biographical article "August Kekulé" by P. E. Verkade of Delft, President of the Organic Section of the IUPAC.[6] It contains a few passing references to Couper, who was otherwise completely ignored by the planners of the symposium.[7]

Ghent. Kekulé was called to the professorship of the University of Ghent in the fall of 1858. That university opened on November 12 an exhibition of Kekulé materials from the period of his stay in Ghent (1858–67). J. Gillis, Professor of Chemistry and Pro-Rector of the university, organized the exhibition and wrote a brief study of Kekulé's Ghent period.[8]

Heidelberg. Kekulé was *Privat-Dozent* in Heidelberg from 1856–58. There he worked in a privately furnished laboratory because Bunsen who held the chair of chemistry at the university refused to let men of Kekulé's rank use the Chemical Institute for research! On November 30, 1957, Heinz A. Staab delivered an inaugural address entitled "A Hundred Years of Organic Structural Chemistry."[9] He reviewed the development of the structural theory since 1857, discussed the achievements and limits of classical structural chemistry, and ended with an analysis of the potentialities of modern structural studies. He emphasized the distinction between the statics and dynamics of moleculed and the still very enigmatic position of the concept of a "transition state."

The Continued Neglect of Couper

Reviewing these celebrations and their origin, the relative neglect of Archibald Scott Couper is remarkable. At least the Chemical Society, one would have imagined, would have insisted on Couper's equal claim with Kekulé as an originator of the Structural Theory. Richard Anschütz's monumental efforts to restore Couper to his deserved eminence seem once more to have been ignored.[10]

Undoubtedly Couper originated with Kekulé the basic tenets of the structural theory. Couper's paper was commented on by Butlerov and Kekulé, while Wurtz, his teacher, was also influenced by him. But his claim to fame is further strengthened by other contributions made in 1857–58. He was the pioneer in the use graphical formulas for organic compounds, using lines to join the atoms.[11] He wrote a ring formula for cyanuric

[1] Supported by National Science Foundation Grant G-4207.

[2] KEKULÉ, A., *Ann.*, **106**, 129 (1858).

[3] *Compt. rend.*, **46**, 1157 (1858). The title pages of these two articles are reproduced in THIS JOURNAL, **36**, 106, 107 (1959).

[4] BROWN, H. C., J. CHEM. EDUC., **36**, 104 (1959).

[5] For an analysis of the failures of the structural theory *cf.* O. T. BENFEY, J. CHEM. EDUC., **34**, 286 (1957).

[6] Also in *Proc. Chem. Soc.*, **1958**, 205.

[7] A summary of the symposium was published in the *Proc. Chem. Soc.*, **1958**, 298. The full text of lectures and papers will be published for the International Union by Butterworths, London, in 1959.

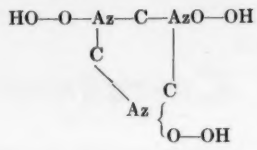
[8] *De Brug*, II, No. 2, 65–75, (April-June 1958); available as a separate issue from the University of Ghent, Belgium.

[9] The complete text appeared in *Angew. Chem.*, **70**, 37–41 (1958).

[10] *Cf.* L. DOBBIN, "The Couper Quest," J. CHEM. EDUC., **11**, 331 (1934).

[11] It is of interest that Wm. Higgins much earlier used lines for a similar purpose, but his approach was never followed up in organic chemistry; *cf.* E. R. ATKINSON, J. CHEM. EDUC., **17**, 3 (1940).

acid (O=8)[12] seven years before Kekulé conceived of a cyclic arrangement of atoms (for benzene), and he advocated the necessity of variable valences against Kekulé's determined opposition. Experimentally he was one of the early workers to become aware of the lack of reactivity of benzene and was the first to synthesize bromo- and *p*-dibromobenzene. Following on Wurtz's successful conversion of ethylene dibromide via the diacetate to ethylene glycol, Couper had thought to convert the seemingly highly unsaturated benzene to the corresponding glycol. He discovered that bromine vapor attacked by substitution rather than addition, that it attacked very slowly, producing the mono- and dibromo derivatives, and that the products were remarkably inert to silver acetate.[13] Finally he used the term "structure" by analogy with its use in linguistics, to signify order and arrangement of atoms rather than spatial distribution, thus accurately recognizing the topological as contrasted with a geometrical character of the original structural theory.[14,15]



[12] *Ann. chim. phys.* (3), **53**, 489 (1858); reprinted by R. Anschütz in *Proc. Roy. Soc. Edinb.*, **29**, 265 (1909). English Version in Alembic Club Reprint No. 21, Edinburgh, **1953**, p. 33.
[13] *Compt. rend.*, **45**, 230 (1857).
[14] *Cf.* SENIOR, J., J. CHEM. EDUC., **15**, 464 (1938).
[15] BENFEY, O. T., "Archibald Scott Couper" in "Lives of Great Chemists," Eduard Farber, Editor; Interscience, in press.

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The Experimental Basis of Kekulé's Valence Theory

Between 1850 and 1892 August Kekulé (1829–96) published over a hundred papers. The majority of these were experimental communications in organic chemistry and related topics.[1] Even a superficial examination of the papers shows that Kekulé's knowledge of the chemistry of his day was extraordinarily comprehensive. We can readily accept his claim that he had studied the historical development of chemistry from the time of his first acquaintance with chemistry, and that he had spent a good deal of time mastering its classics before he accomplished anything on his own. Indeed, he maintained that prior to the time of any of his theoretical papers his friends had considered his fund of chemical knowledge more reliable then Berzelius' *Jahresberichte*.[2] Thus we learn, from an analysis of his papers, that he attacked his own specific research problems only after having virtually mastered all the related chemical literature on the subject. In addition, in many instances, his papers reveal rather precisely how the work of previous investigators provided him with a point of departure for his own experiments, or how another author's work was corrected, challenged, expanded, or reinterpreted to explain a new situation. Characteristically, the complete and considerate recognition of the labors of his predecessors formed an integral part of all his published works. The list of chemical investigators who benefited directly from Kekulé's various activities on some point of technical detail, over a period of some forty fruitful years, is impressive indeed. That subject would merit a full study by itself.

Hardly less important for the evaluation of Kekulé's over-all contribution is the observation that his most significant discoveries taken together exhibit great overall unity. This was the result of his remarkable command over a great and complex mass of factual experi-

Presented as part of the Kekulé-Couper Centennial Symposium on the Development of Theoretical Organic Chemistry before the Division of History of Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

[1] ANSCHÜTZ, RICHARD, "August Kekulé," 2 vols., Verlag Chemie, Berlin, **1929**: Vol. I, Leben und Wirken; Vol. II, Abhandlungen, Berichte, Kritiken, Artikel, Reden. The second volume contains 75 papers authored by Kekulé, 28 papers coauthored by Kekulé and 28 other items including book reports, technical comments and speeches, in German, French, and English. Anschütz was a student and colleague of Kekulé's for 21 years and his successor in Bonn in 1898. At the *Versammlung Deutscher Naturforscher und Aerzte* in 1896, the year of Kekulé's death, Emil Fischer urged Anschütz to write a detailed obituary notice for the *Berichte*. The eventual outcome of this request was a two volume biography and collection of papers published 33 years later on the 100th anniversary of Kekulé's birth. Since 1929 these volumes have been the most indispensable and reliable single guide for all Kekulé studies. Passages quoted from the works of Kekulé have been translated by the author of this paper.

[2] Vital information on the earliest period of Kekulé's chemical career is available in two speeches which he delivered toward the end of his life: the first in 1890 at a *Kekuléfeir* sponsored by the Deutsche Chemische Gesellschaft in Berlin (*Ber.*, **23**, 1265–1312 (1890) and Anschütz II, 937–47); the second in 1892 at the Chemical Institute in Bonn on the occasion of the 25th year of his professorship there (Anschütz, II, 947–52).

mental information concerning the properties and reactions of individual organic compounds, coupled with a passionate search for some organizational principle which would shed new light upon the question of the molecular consitution of organic compounds in terms of certain well-known and characteristic reaction types. Even Kekulé's earliest works contained refreshingly straightforward attempts to give an answer to that question, and eventually he provided one of the most explicit nineteenth century formulations of a chemical philosophy on the whole broad subject of molecular constitution.

Kekulé was twenty-nine years of age when he formulated the valence theory which provided a great new stimulus to theoretical organic chemistry. We may well emphasize at the outset that he was not led to the theory because of any specific experimental discoveries. It was an organizational achievement accomplished in its concise final form by a few deft strokes of the pen—a mere sentence or two. The theory was simple, and its value was almost immediately obvious to most chemists. All of the specific experimental information which Kekulé marshalled together in support of his valence theory in the famous statement of 1858 must have been available to a great number of eminently competent contemporary chemists, but the fact remains that only he and Couper were able to suggest the crucial theoretical concepts which laid the foundation for modern structural organic chemistry.

It is the object of this paper to discuss the experimental basis of Kekulé's valence theory of 1858 as seen in the progressive stages of his own experimental career prior to that time. An adequate exposition of Kekulé's theoretical papers of 1857/8[3] would require a great deal more time than is available here, and we shall do no more than to indicate where his experimental work bears directly on the theory of the quadrivalency and self-linking characteristics of carbon.

Darmstadt and Giessen (1848–51)

Kekulé remarked late in life that it had been Liebig's chemistry lectures which had enticed him to abandon a planned career of *studiosus architecturae*. Between 1848 and 1851 he studied analytical chemistry in the Darmstadt Technical School with Friedrich Moldenhauer, and in Giessen with Heinrich Will and Theodor Fleitmann (discoverer of sulfur matches). In addition he attended Liebig's lectures in experimental, theoretical, and agricultural chemistry, Kopp's lectures on crystallography, stoichiometry, and mineralogy, Knapp's lectures on chemical technology, and Strecker's lectures on organic chemistry. His first experimental communication was a carefully performed but routine analytical investigation on amyl sulfuric acid, its salts and their distillation products; it was sponsored by Heinrich Will in Giessen in 1850 and became his doctoral dissertation.[4]

The only Kekulé work on record from Liebig's private laboratory was an analysis of gluten and wheat bran.[5] Liebig's continued influence upon Kekulé's chemical views was probably not very great. The two men were never on very congenial terms with one another. Kekulé in the 1850's praised Liebig highly, but presumably because he needed his recommendation in order to obtain a professorial chair in chemistry in a German university. That was something Kekulé wanted above all else. By 1850 Liebig had more or less abandoned his active interest in organic chemistry for agricultural and physiological chemistry, and thereafter no longer kept up in his lectures with the newer theoretical developments. While Liebig was dogmatic in his pronouncements, Heinrich Will in his lectures on organic chemistry radiated a noncommittal attitude on the question of the consitution of organic compounds. Reinhold Hoffmann, one of Kekulé's most intimate student associates at Giessen, wrote later: "At that time already in our circles the sentiment was aroused, partly unconsciously, that the rigorous radical theory was not the all-redeeming dogma of chemistry."[6]

Paris (1851–52)

In 1851 Kekulé left Giessen to undertake further studies in Paris. Liebig had told him that in Paris he would extend his horizons, learn a new language, and experience the great city, but learn no chemistry. Concerning the latter, Liebig could not have been more in error. While en route to Paris, Kekulé was absorbing Charles Gerhardt's *Introduction à l'étude de chimie par le système unitaire* (Paris, 1848).

In Paris Kekulé attended lectures at the Sorbonne, the Ecole de Médicine, the Conservatoire des Arts et Métiers and the Collège de France. He listened to the lectures of Dumas, Cahours, Wurtz, Payen, Magendie, Regnault, and Pouillet. It was by chance that he met Charles Gerhardt in Paris. Their first conversation lasted twelve hours and thereafter they met at least twice every week for over a year. Much of that time was spent in weighing Gerhardt's various proposals for schemes of classification of organic compounds, the overall object being to try and account for a number of series of compounds on the basis of a single type theory. The close association with Gerhardt in Paris was later to have the profoundest effect upon the direction of Kekulé's theoretical ideas.[7]

Switzerland (1852–53)

In 1852 Kekulé became for one and a half years the private assistant to the chemist Alfred von Planta in Reichenau/Chur, Switzerland. In this beautiful, secluded and idyllic mountain spot Kekulé expected to rework and rethink his newly acquired scientific information; and especially, as he later remarked, that portion of it which he had learned from studying the manuscript of Gerhardt's as yet unpublished famous

[3] The two crucial theoretical papers were: "Ueber die s. g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale," *Ann.*, **104**, 129–50 (1857); "Ueber die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," *Ann.*, **106**, 129–59 (1858).

[4] KEKULÉ, "Ueber die Amyloxydschwefelsäure und einige ihrer Salze," *Annalen*, **75**, 275–93 (1850).

[5] LIEBIG, *Chemische Briefe*, 3rd ed., Heidelberg, **1851**, Letter No. 28, pp. 592, 595.

[6] ANSCHÜTZ, I, 16–17.

[7] GRIMAUX, ED., AND GERHARDT, CH., *Charles Gerhardt, sa vie, son oeuvre, sa correspondence, 1816–1856*. Document d'histoire de la chimie. Paris, 1900. This volume gives a very full account of Gerhardt's theory of types and of its connection with the chemical activities of Williamson, Chancel, Wurtz, Odling, Dumas, Frankland, Hofmann, Kopp, and Kekulé. For the years of friendship between Gerhardt and Kekulé (1851–56) see esp. Pt. I, Chaps. VII and VIII and Pt. II, Chaps. VI and VII.

four volume *Traité de chimie organique* (Paris, 1853–56). Concerning this time of his life Kekulé adopted for himself the sentence from Heine: "Mein Kopf war damals ein zwitscherndes Vogelnest von confiscierlichen Büchern."

Four joint publications with Planta appeared between 1853 and 1854. Two of these dealt with the quantitative analysis of gallstones and a number of minerals. More important were the two papers on the volatile alkaloids, nicotine and coniine, whose study was then of obvious interest in light of A. W. Hofmann's discovery in 1851 of the mode of formation of primary, secondary, and tertiary amines, and the quaternary ammonium bases. Kekulé in later life never again returned to the investigations of the alkaloids, but it is worth noting, first, that this work put him in contact with Gerhardt once more,[8] and second, that all of these papers indicate that Kekulé had mastered the earlier literature on the subject—a characteristic exhibited by every paper that he ever published.

London (1853–55)

In 1853, upon the recommendation of Liebig, Kekulé reluctantly accepted a private assistantship at St. Bartholomew's hospital in London in the laboratory of Liebig's former student, Professor John Stenhouse.[9] Bunsen had advised him to go to London to learn a new language, even, if no chemistry. Bunsen turned out to be just as mistaken about Kekulé's sojourn in London as Liebig had been about his stay in Paris two years earlier. For, in London, Kekulé almost immediately joined a friendly circle of former Giessen students who spent a good part of their time in vigorous discussions on the new theoretical chemistry of Gerhardt, Laurent, and Kolbe. Before long Kekulé's acquaintances in London included Hugo Müller who had been a student of Wöhler's in Göttingen, A. W. Hoffmann, Thomas Graham, Edward Frankland, William Odling, and in particular Alexander Williamson who was Professor of Practical Chemistry in University College, London. Kekulé's roommate in London, Reinhold Hoffman, who was then employed as an assistant in Williamson's laboratory, wrote to Anschütz that many of the ideas which Kekulé acquired at that time in London only became prominent in his later work; such for example were his persistent attempts to reduce the properties of organic compounds and radicals to the elements themselves. By refusing to accept the radicals or the various types as something absolute, Kekulé was not far removed, thought Hoffman, from the idea that "in the organic compounds, only the valences of carbon are decisive for the combining ability with other elements and groups of atoms and for the transformability of the compounds."[10]

Kekulé's work under Stenhouse was routine and unchallenging, but fortunately interrupted by frequent visits to University College. There he felt himself drawn into the excitement of the chemical disputes which were being conducted by Williamson and his colleagues against Hermann Kolbe on the question of the theory of formation of water, ethers, and acids. Williamson's mixed ether experiments of 1850/52[11] had already indirectly provided a demonstration of the views of Laurent and Gerhardt regarding the equivalents to be used in writing the formulas for alcohol and ether. The production of mixed ethers being derived from two alcohols, Williamson represented ether as the oxide of the two ethyl groups, and alcohol as the oxide of ethyl and hydrogen.

Williamson's notion of chemical formulas, written so as to exhibit their chemical constitution through the arrangement of interdependent atoms, was first developed in his paper of 1852: "On the Constitution of Salts."[12] His use of bivalent oxygen for linking together hydrogen and hydrocarbon radicals was limited essentially to compounds of the water type. Odling and Frankland extended the idea to elements other than oxygen as the linking agent, and Gerhardt added other types to Williamson's water type but the latter were mere "types of double decomposition" without the structural significance of Williamson's conception.[13]

Kekulé, who was in close contact with Williamson and in the midst of discussions related to all of these matters, soon arrived at the idea of using phosphorus sulfide to replace the oxygen in organic acids and esters with sulfur. This was after Cahours had already succeeded in replacing the oxygen of monocarboxylic acids with chlorine by means of phosphorus pentachloride. When Kekulé communicated his ideas to Williamson the latter suggested that if he did not undertake the experiments immediately he would attempt them in his own laboratory. Kekulé's position under Stenhouse did not easily lend itself to private investigations. Nevertheless he began the experiments at St. Bartholomew's in the early morning hours, much to the consternation of Stenhouse who had no difficulty in discovering from the sulfurous odors that something foreign to his specific research concerns was going on in his own private laboratory. Kekulé's paper "On a new Series of Sulphuretted Acids" was handed in to the Royal Society of London by Williamson and delivered there in April of 1854 by Kekulé under the presidency of Graham.[14]

Kekulé introduced his paper as follows:

> Adopting the idea that the series of organic compounds, of which sulphuretted hydrogen is the type, corresponds in every respect with the series of which water is the type, I concluded that not only mercaptans and neutral sulphides, which correspond to the alcohols and ethers, but also compounds corresponding to the acids, anhydrous acids, and ethers of acids might be produced; I therefore endeavoured to obtain reactions which would enable me to replace oxygen in the compounds of the latter series by sulphur.

By fusing amorphous phosphorus and sulfur in an atmosphere of carbonic acid Kekulé produced the tersulfide (P_2S_3) and the pentasulfide (P_2S_5), and demonstrated that they acted on the members of the water series in a manner analogous to the action of the corresponding compounds of phosphorus and chlorine (PCl_3

[8] Anschütz, I, 33–35.

[9] Kekulé said later, "Aber ich hatte wenig Lust anzunehmen, weil ich ihn, [Stenhouse] wenn ich mir den Ausdruck gestatten darf, für einen Schmierchemiker hielt." Anschütz, II, 950.

[10] Anschütz, I, 41.

[11] Williamson, A. W., "Theory of Etherification," *Phil. Mag.* [3], **37**, 350–56 (1850); "On Etherification," *J. Chem. Soc.*, **4**, 229–39 (1852); See also Alembic Club Reprints, No. 16 for papers by Williamson, and cf. Chancel, G., "Sur l'éthérifaction et sur une nouvelle classe d'éthers," *Compt. rend.*, **31**, 521–23 (1850).

[12] Williamson, A. W., *J. Chem. Soc.*, **4**, 350–55 (1852).

[13] Divers, Edward, Obituary Notice for Williamson, *Roy. Soc. Proc., London*, [A], **78**, xxiv–xliv (1907).

[14] Kekulé, *Proc. Roy. Soc., London*, **7**, 37–40 (1854); more detailed German version in *Ann.*, **90**, 309–16 (1854); abridged French version in *Annales de chimie*, [3], **42**, 240–42 (1854).

and PCl_5), although less violently. But there was this difference,

> . . . that by using the chlorine compounds the product is resolved into *two* groups of atoms, while by using the sulphur compounds there is obtained only *one* group; a peculiarity, which, according to the dibasic nature of sulphur, must have been expected. . . . By acting on these compounds of sulphur and phosphorus with water, one atom of sulphuretted hydrogen is obtained, while the chlorides give two atoms of hydrochloric acid.

Kekulé then listed the series of sulfuretted organic compounds obtainable from hydrogen sulfide, indicating that they were precisely analogous to the compounds corresponding to the water type, viz.: "mercaptan,"

$$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\}S$$

and "sulfide of ethyl,"

$$\left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\}S$$

which could be obtained by reacting alcohol or ether with pentasulfide of phosphorus; or as had been demonstrated previously in the literature, by replacing one or two atoms of hydrogen or of metal with organic radicals in sulfuretted hydrogen, sulfide of potassium, or sulfide of hydrogen and potassium. He furthermore prepared "othyl hydrosulfuric acid" (also called "thiacetic acid"),[15]

$$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}S$$

by the action of tersulfide of phosphorus on monohydrated acetic acid or of pentasulfide of phosphorus on fused acetate of soda. Similarly, "othyl-sulfide of othyl" (also called "thiacetic acid anhydride" or "anhydrous sulfuretted acetic acid"),

$$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\}S$$

was prepared by heating pentasulfide of phosphorus with anhydrous acetic acid. He also reported "othyl-sulfide of ethyl" ("thiacetic acid ether"),

$$\left.\begin{matrix} C_2H_3O \\ C_2H_5 \end{matrix}\right\}S$$

in which he was later shown to have been mistaken.

The more detailed German version of this paper of 1854 was more decidedly on the side of Gerhardt and Williamson against Kolbe in the manner of writing formulas. While Kekulé remarked that he had not intended his formulas to be an exact representation of the facts, since he was uncertain about the intermediate products, he nevertheless had no reservations about adopting the Gerhardt formulas based on an "equivalent" of carbon equal to 12, i.e., consistent with the formula H_2O for water in place of HO or $\left\{\begin{matrix} HO \\ HO \end{matrix}\right\}$ which latter would follow from the use of an "equivalent" of 6 for carbon.[16] Kekulé argued that according to the HO view, alcohol and ether ought to be written

$$\left\{\begin{matrix} C_4H_5O \\ HO \end{matrix}\right\} \text{ and } \left\{\begin{matrix} C_4H_5O \\ C_4H_5O \end{matrix}\right\}$$

respectively. But how would one then account for the observation that the sulfide of phosphorus produced alcohol mercaptan,

$$\left\{\begin{matrix} C_4H_5S \\ HS \end{matrix}\right\}$$

while the chloride of phosphorus gave ethyl chloride, C_4H_5Cl, + HCl in place of

$$\left\{\begin{matrix} C_4H_5Cl \\ HCl \end{matrix}\right\}$$

All of these matters were explained perfectly, thought Kekulé by assuming "that the amount of chlorine equivalent to a single indivisible atom of oxygen is divisible by 2, while the sulfur, like oxygen itself, is *dibasic*, so that 1 atom is equivalent to 2 atoms of chlorine."

Gerhardt, Williamson, Hofmann, and Stenhouse all recognized the importance of Kekulé's experimental investigation in the preparation of the sulfuretted organic acids, and they praised the work highly.[17] In effect, Kekulé's paper helped to confirm Williamson's formula for acetic acid, according to which the oxygen was shared between hydrogen and "othyl," (C_2H_3O); for he had shown that the phosphorus sulfides when allowed to act upon acetic acid or its anhydride or ester, produced substances in which only half of the oxygen was replaced by sulfur.

Now if we accept at face value the statements in 1890 of the 61-year-old Kekulé reminiscing about his days in London[2] then we are led to believe that in the year of this paper on sulfuretted acids he was already preoccupied with the fundamentals of his valence theory, i.e., four years before he put any such ideas into any of his papers. According to his own account, which he said contained the "most indiscrete disclosures from my inner life," the first visions of the structural theory came to him while dozing on the outside deck of an om-

[15] "Othyle" for "oxygen-ethyle" had been introduced by Williamson for the acid radical C_2H_3O. (*J. Chem. Soc.*, **4**, 238 (1852)). Gerhardt called the same radical "acétyle" (*Annales de chimie*, [3], **37**, 339 (1853)). Kekulé preferred to reserve the name "acetyl" for C_2H_3 and so he accepted Williamson's "othyl."

[16] Gerhardt, Laurent, Chancel, and Williamson had by this time all supported the H_2O view, (H = 1, O = 16, C = 12, S = 32) against the HO view (H = 1, O = 8, C = 6, S = 16), which latter was so long defended by Kolbe and others.

[17] Gerhardt wrote that Kekulé's paper had produced a great sensation in the chemical world by opening up a novel way of scientific investigation. The facts and new substances discovered by Kekulé, he wrote, were of such a nature as to contribute considerably to the discussions of certain fundamental questions with which contemporary chemists were occupied. Williamson wrote: "Dr. Kekulé unites great intellectual acuteness and power of generalization with a singularly profound and complete acquaintance with chemical science. . . . The last research of Dr. Kekulé on a new series of organic acids has opened up to science an entirely new field for investigation. . . . These brilliant researches have gained Dr. Kekulé an European reputation among scientific chemists. . . ." Hofmann wrote, "Seine Untersuchung, welche aus einer consequenten Durchführung der Gerhardt'schen Anschauungsweise geflossen, hat die Chemiker mit einer Reihe höchst merkwürdiger Verbindungen bekannt gemacht, deren Existenz in dem System klar gegründet ist, deren Darstellung aber bis jetzt nicht gelungen war." Even Stenhouse attributed to Kekulé an excellent familiarity with theoretical and practical chemistry, but especially "with the views of the more modern French school." See letters in behalf of Kekulé's intended candidature at Zürich, Anschütz, I, 55–58.

nibus after a strenuous evening of chemical discussions with his friend Hugo Müller in London. Diminutive atoms gamboled before his eyes, the smaller ones uniting to form pairs, the larger ones embracing the smaller ones and dragging them behind in a whirling giddy dance. "Thus, the structural theory came into being." But two of Kekulé's friends at Heidelberg "shook their heads in doubt" when he developed his ideas on paper for them. So he quietly put his manuscript in the drawer: "Nonumque prematur in annum." He needed more time to test those dreams "by the awakened understanding."

Kekulé was obviously in no hurry to publish his ideas, but he was constantly preoccupied with them. Von Baeyer remarked in Munich in 1905,[18] on the occasion of his 70th birthday, that while his own motivation for chemical research had been "whatever was fun," his teacher Kekulé was a "born chemical general" who wanted to "command nature." Baeyer said concerning himself: "I did not carry out my experiments to see whether I was right, but to see how substances are related to one another." In contrast, he characterized Kekulé's attitude as one which was basically critical, and directed mainly toward the reorganization of a "mighty amount of material." "Kekulé," said Baeyer, "had no interest in substances themselves, but was only concerned whether they conformed to his ideas. When that was the case, it was fine; if not, they were rejected."

Two years after his famous 1890 speech in Berlin Kekulé was speaking to another audience in Bonn on "selected chapters (aphorisms) from the history of chemistry."[2] He remarked that "age makes one gossipy, and the old are inclined to speak much about themselves." On that occasion he mentioned again that his theory of valency and the structural chemistry had originated in his thinking during his stay in London. He said, "Such ideas were then in the air, [and] sooner or later they would have been expressed; perhaps a year or two later, perhaps in another way than I did." Kekulé went on to attribute his success, both to a preoccupation with architecture, which had led him to think about the spatial representation of atom groups, and to his manifold travels from which he had learned how to separate the good from the bad. He remarked, "I had become an eclectic. I was not captured by the spirit of a narrow school." From Liebig's pupil, to an adherent of the chemical philosophy of Dumas, Gerhardt, and Williamson, Kekulé had become, so he said, a proponent of no school at all. He had become a critic of the theory of types and of compound radicals.

Kekulé made these statements some 32 to 34 years after he had enunciated his valence theory. He was then world famous for it. We might suggest that his views in the 1854 paper were noticeably oriented in the direction of valency considerations, but they certainly were not explicit. Let us then examine some of the experimental investigations which he completed prior to 1858 but in the period after he left London.

Heidelberg (1856–58)

In 1855, after Kekulé had failed to obtain the candidature for the professorial chair of pure chemistry at the Polytechnic School of Zürich, mostly because Liebig would not recommend him for it, he sought formal admission to an academic lectureship in the faculty of a German university. He eventually chose Heidelberg believing that he would be able to draw large classes in organic chemistry there. Bunsen, who was in charge of the largest laboratory in all of Germany, had by 1855 turned all of his attention to analytical, inorganic, and physical chemistry at Heidelberg and so organic chemistry more or less fell into Kekulé's lap. It did not take long for the unaffected and congenial Kekulé, who was an irresistible academic lecturer, to capture an enterprising group of young men who later distinguished themselves in some branch of chemistry. Among those who were in Heidelberg at the time were Emil Erlenmeyer, Adolf von Baeyer, Hans Landolt, Freidrich Beilstein, Lothar Meyer, Alexander M. Butlerow, and Henry E. Roscoe. Kekulé could speak to the English, French, and Italians in their native tongues, and he knew quite well what was going on in their own countries, chemically speaking.

Lothar Meyer relates[19] what an exciting place Heidelberg was at that time for chemists. Gerhardt's *Traité* was in the process of being published, but the fourth volume containing the key to Gerhardt's whole chemical system had not yet appeared when Kekulé arrived in Heidelberg early in 1856. Kekulé, the young *Dozent*, was an eager apostle of Gerhardt's type theory, and initiated debates against the authority of the traditional dualistic theory which lasted for hours and days, and in which he won his ground point for point. His great dismay was that the inorganic chemists had not yet freed themselves from "the swindle of electro-chemical-dualistic addition."[20] The names of Gerhardt and Williamson were constantly referred to during the organic chemistry lectures, which he delivered with "wahrer Liebhaberei"—so he wrote Williamson in 1856.

Adolf von Baeyer, who left Bunsen's laboratory to join Kekulé in his small one-window laboratory, spoke of the latter as the "Reformator der Chemie," who with his French and English ideas opened up a new world in theoretical chemistry. In his *Erinnerungen aus meinem Leben*[21] Baeyer wrote:

> Charmed by the logical consistency of the new theory, which later was baptized as the structural theory, he [Kekulé] constructed, before his enthusiastic listeners, the structure of theoretical chemistry in which we still live today. And even if the fundamental idea of interpreting the types by the valence of the atoms was started by Williamson, and if Couper simultaneously pronounced the tetravalency of carbon, he still has the glory of having founded a unitary system of organic chemistry and having proclaimed it to the world with the enthusiasm of a prophet.

Anschütz has examined a 400-page notebook of a student who attended Kekulés lectures on organic chemistry in the winter semester of 1857/58.[22] It contains a 39-page section entitled "Konstitution und Systematik der organischen Verbindungen," and an appendix with an historical treatment of Gerhardt's type theory. Noteworthy is the fact that Kekulé was then already using the graphic formulas which he introduced into the

[18] Vorfeier des 70. Geburtstages von Adolf von Baeyer, *Z. für ang. Chemie*, **18**, 1617–22 (1905).

[19] MEYER, LOTHAR, Obituary notice for Leopold von Pebal, *Ber.*, **20**, 1000 (1887).

[20] Letter to Williamson, November 1856, Anschütz, I, 70/1.

[21] BAEYER, A. VON, *Gesammelte Werke*, 2 Vols., Braunschweig, 1905, I, xv.

[22] Anschütz, I, 71–72.

first issue of his *Lehrbuch der organischen Chemie* (Erlangen, 1859), in which the mode of union of the atoms in the molecules are made clear.

Kekulé's first experimental communication from his private laboratory in Heidelberg, a paper on the constitution of the fulminate of mercury, was delivered in January of 1857 to the newly-founded *Naturhistorisch-medizinischer Verein* of Heidelberg.[22] By 1857 fulminic acid and the fulminates had been the subject of numerous investigations for over half a century. Howard, Berthollet, Gay-Lussac, Liebig, Berzelius, and Gerhardt had initiated important work on the subject. Gerhardt in his *Précis* in 1844/5 had suggested that fulminic acid was $C^2H^2N^2O^2$ and that the fulminates belonged to a nitrogenous species having the formula C^2 (H^2X) N where X is equivalent to NO^2. Accordingly the fulminates, thought Gerhardt, should belong to the genus of the cyanides homologous with the normal species designated by C^2H^3N.[24] In his *Traité* of 1854 Gerhardt did not suggest any structure and merely mentioned that while the constitution of fulminic acid was difficult to account for, it seemed reasonable to suppose that it contained NO_2 or NO_4 groups because of its explosive nature.[25] We should note that the Gerhardt formulas given above are based on an equivalent of 12 for carbon, unlike Kekulé's formulas in the discussion which follows.

In Kekulé's investigations the fulminates were subjected to a number of reactions with chlorine and bromine. The experimental details are unimportant here. He concluded that half of the nitrogen contained in fulminate of mercury was present as NO_4, and the other half was combined with carbon as C_2N, giving the formula $C_2(NO_4)Hg$ $Hg(C_2N)$. "This formula," said Kekulé, "indicates at first glance, that the composition of fulminate of mercury shows the greatest analogy with a large number of known substances, to which, e.g., chloroform belongs: C_2 H Cl Cl Cl." Kekulé then listed ten substances with their formulas so arranged as to exhibit a marsh gas-like structure, conforming to the type: C_2 H H H H. He remarked that fulminate of mercury could be looked upon either as nitrated chloroform, i.e., chloropicrin, $C_2(NO_4)$Cl Cl Cl, in which the chlorine had been replaced in part by cyanogen (C_2N) and in part by mercury; or as acetonitrile, i.e., C_2 H H H(C_2N), which had been nitrated and in which both hydrogens had been replaced by mercury. This would make fulminic acid: nitro methyl cyanide, i.e., nitroacetonitril, or $C_2(NO_4)$ H H (C_2N).

In this paper Kekulé introduced a new type—the marsh gas type—which had not been suggested prior to this time except in a paper delivered to the Royal Institution by William Odling[26] in March of 1855, 22 months prior to Kekulé's report to the *Verein* in Heidelberg. Kekulé may not have known about this work although he expressly mentioned another work of Odling's in his theoretical paper of 1857 which we have already mentioned previously.[3]

In that theoretical paper Kekulé stated:

> In order to avoid detailed historical considerations, I mention at the outset, that most of what follows at least does not lay claim to originality; but [it] rather shall be nothing more than a further explanation of the leading ideas, which Williamson has communicated on occasion and which one might call "the theory of polyatomic radicals": ideas, which Odling first extended in his work on the constitution of acids and salts [*J. Chem. Soc.*, **7**, 1–22 (1855)]; which also have been often repeated in German works since Gerhardt adopted these in part in his IVth volume of his *Traité* (without however conceiving them strictly in the sense of Williamson), and whose suitability now most likely can no longer be questioned, since they have led to the discovery of a great number of exceptionally interesting compounds.

We recall that Odling was Williamson's pupil, and that Kekulé's associations with Williamson in London had been very congenial. There seems to be little doubt that Williamson himself was close to similar ideas. He actually deserves considerable credit for the notion of valency, at least in so far as the combining power of radicals is concerned. For as we have shown, he maintained that oxygen held the hydrogen and ethyl radicals together. Still the notion of valency had to be generalized. In particular it needed to be extended to include the element carbon. In this regard Gerhardt was of no help to Kekulé, and it is unlikely that Kekulé arrived at his marsh-gas-like fulminate formulas through any of Gerhardt's views on the subject. Gerhardt had not used marsh gas as a type, but had accepted the formula $C^4H^2H^6$ for marsh gas as Regnault and Dumas had formulated it. In the last analysis even Kekulé was not quite convinced about his proposed structures when he said, "I am far removed from believing that the suggested reasonable formula is proved from the facts which I have communicated for the fulminate of mercury, and will try next, whether new grounds can be produced for my opinion through a synthesis."

In his second paper on the fulminate of mercury,[22] which was delivered eleven months later, (December 1857), Kekulé attempted, on the one hand, to strengthen his previous argument through additional experiments, and on the other, to criticize the recently suggested structure for fulminate of mercury which had been published by the Russian chemist, Schischkoff, who was then working on this same subject in a laboratory in Heidelberg.[27] Kekulé decided in this second paper that by combining some new reactions of his own on fulminate of mercury with information taken from Schischkoff's paper (which we might suggest was superior experimentally but not theoretically to Kekulé's work) that he could add three new items to the list of substances written to conform with his newly designated marsh gas structure. "All these bodies of one series," said Kekulé, "can be included in one mechanical type; all contain the same number of atoms if one considers the nitro-group $[NO_4]$ and the cyanogen $[C_2N]$ as radicals analogous to the elements; at the same time they

[22] KEKULÉ, "Ueber die Constitution des Knallquecksilbers," *Ann.*, **101**, 200–13 (1857); **105**, 279–86 (1858).

[24] GERHARDT, C., *Précis de chimie organique*, 2 vols., Paris, 1844/45. I, 382–84; II, 445.

[25] GERHARDT, C., *Traité de chimie organique*, Vol. 2, 384, Paris, 1854.

[26] ODLING, W., "On the Constitution of the Hydro-carbons," *Roy. Inst. of G. Brit., Proceedings*, **2**, 63–66 (1854–58).

[27] SCHISCHKOFF, L., *Ann.*, **101**, 213–17 (1857). We notice that Kekulé's first paper on fulminate of mercury and Schischkoff's paper were both submitted to Liebig on December 26, 1856; they were published consecutively in the *Annalen*. But this was not done until after Liebig, as editor of the *Annalen* had recommended in a letter to Kekulé (Anschütz, I, 74) that the two men publish their investigations jointly as he and Wöhler had done—which suggestion Kekulé did not follow. See also CHICHKOFF, "Sur la constitution de l'acide fulminique et une nouvelle série de corps dérivés de l'acide acétique." *Ann. chim., Paris*, [3], **49**, 310–38 (1857).

exhibit great differences in their individual properties, being occasioned by the differences in dynamic nature of the elements which have entered into them."

There is one thing about these two Kekulé papers on the fulminates which is peculiarly puzzling. It is that Kekulé made use of the Kopp-Gmelin-Dumas-Liebig equivalents instead of the Gerhardt-Williamson equivalents. Thus he wrote C_2H_4 for marsh gas, instead of CH_4; and $C_4H_2N_2O_4$ for fulminic acid instead of $C_2H_2N_2O_2$, etc. Let us recall that in his experimental paper on thiacetic acid, written two years earlier and discussed above,[14] and in the theoretical paper of 1857[3] which falls between the two papers on fulminate of mercury, Kekulé adopted the Gerhardt-Williamson view.

The question which automatically presents itself is whether Kekulé was converted during this time to the older view. It is more plausible to suppose, as Anschütz suggests,[28] that Kekulé was making a concession in conforming to familiar German usage, so that the chemists who would be reading his papers in Liebig's *Annalen* would find the formulas to be in agreement with the editor's own usage and would thus be in a position to judge more readily the value of his work when placed alongside that of Schischkoff's paper on the same subject in the same issue of the *Annalen*. In an unpublished manuscript Kekulé says as much.

The situation with respect to equivalents is also clarified considerably on examining Gerhardt's views. In the *Précis* of 1844/45 Gerhardt used only the newer system of atomic weights (O = 16, C = 12), yet a decade later he used the older system (O = 8, C = 6) in the first three volumes of his *Traité* (1853–56). Then in the fourth volume of that work, published posthumously in 1856, Gerhardt reintroduced his original system in order to spell out the theoretical foundations of the preceding three volumes. Gerhardt, in that volume, clearly stated that his own private position had been consistent all along.[29] He too had apparently conformed to familiar usage. Kekulé could very well have been the only adherent of the Gerhardt-Williamson views in Germany in 1857/58.

One final observation in the light of the above remarks. It may not be unreasonable to suppose that the formulas according to which Kekulé arranged the fulminates by mechanical type analogous to the structure of methane, represent a first theoretical attempt on his part to test the notion of the quadrivalence of carbon. This is accomplished by replacing each C_2 by a C in his formulas. I am suggesting that Kekulé may well have conformed to familiar formula usage by writing C_2's (where C = 6) while holding on to his own mental picture of C's (where C = 12). At least so it seems in retrospect. And even beyond that one might note that in those cases where there are more than two C_2's per formula,[30] that Kekulé was on the threshold of the idea of the self-linking of carbon. This would require that each C_2 be replaced by a C and that one designate, in addition, a feasible graphical scheme to show the linkage.

It goes without saying, that the theoretical importance of these two fulminate papers for the growth of Kekulé's valence theory stands, even if we now know that the fulminates have no such structure as he imagined. The final clarification on the question of the structure of the fulminates began in the 1880's and was only completed by John Ulric Nef of the University of Chicago, who proved the carbyloxime structure in 1894.

We must still provide brief comments to the other experimental papers which Kekulé completed in Heidelberg by 1858 before he left for Ghent. A paper on the formation of glycolic acid from acetic acid was delivered to the Heidelberg *Verein* on March 1858.[31] The theoretical importance of this work was that the product obtained from boiling the barium and calcium salts of monochloroacetic acid was identical with glycolic acid which had been obtained by other means. There were not two different modifications as Wurtz had contended. In this paper we also find the beginning of Kekulé's classification of the alcohols and the carboxylic acids as given in the *Lehrbuch* of 1859. Remember, however, that in his paper on glycolic acid, as well as in his papers on fulminate of mercury, Kekulé used the old style formulas written to correspond to the "equivalents" of common usage.

More important, Kekulé recognized this as "the first example of the formation of a *diatomic* (zweiatomig) acid from a *monatomic* (einatomig) acid, of the acetic acid group; in the series of these acids, being precisely what the formation of glycol from alcohol is to the series of the corresponding alcohol." In other words, Kekulé drew attention to the analogy which exists between alcohol and acetic acid when compared respectively with glycol and glycolic acid, in so far as alcohol and acetic acid are both transformed in the process from "monatomic" to "diatomic" substances by the substitution of a diatomic oxygen atom for a monatomic hydrogen atom. In two later theoretical papers of 1857/8 Kekulé demonstrated how to construct a whole structural system of organic chemistry on the basis of experimentally determined substitutions of monatomic atoms by diatomic, triatomic, and tetratomic atoms or groupings.

Three other experimental papers originated in Kekulé's laboratory in Heidelberg. One of these was on "chloralid," which was first identified by Wallach in 1875 as trichlorolactic acid ethylidene chloride ether. The other two papers were on chemical physiology. The first of these, on saccharification in the liver, was an investigation in which Claude Bernard's *matière glycogène* was prepared in pure form and analyzed. The

[28] Anschütz, I., 85–86; Graebe, C., *Geschichte der organischen Chemie*, Berlin, **1920**, p. 180.

[29] Gerhardt, C., *Traité de chimie organique*, Vol. 4, Paris, **1856**, p. 586, "Quelques chimistes cependant, saisissant mal ma pensée, supposent à mes types la même signification qu'aux types moléculaires sur lesquels M. Dumas a développé, il y a longtemps déjà ["Mémoire sur la loi des substitutions et la théorie des types," *Comptes Rendus*, **10**, 149 (1840)] des spéculations fort ingenieuses; mais je dois réclamer contre cette assimilation, quelque précieux qu'un si haut patronage puisse être pour le succès de mes vues; car à la vérité, il n'y a de semblable que le nom, emprunté à la langue vulgaire, et mes types signifient tout autre chose que les types de M. Dumas, ceux-ci se rapportant à l'arrangement supposé des atomes dans les corps, arrangement qui, dans mon opinion, est inaccesible à l'experience. Mes types sont des *types de double décomposition*."

[30] As in Kekulé's fulminic acid, $C_2(NO_4)H\ H(C_2N)$; fulminate of mercury, $C_2(NO_4)Hg\ Hg(C_2N)$; acetonitrile, $C_2\ H\ H\ H(C_2N)$; and trichloroacetonitrile, $C_2\ Cl\ Cl\ Cl(C_2N)$.

[31] Kekulé "Bildung von Glycolsäure aus Essigsäure," *Verhandlungen des naturhistorischmedizinischen Vereins zu Heidelberg*, **1**, 105–107 (1857–59); *Ann.*, **105**, 286–92 (1858).

other paper, by Friedrich and Kekulé, was on the degeneration of the so-called amyloids (starches) of the spleen. None of these papers need concern us further here, but they do indicate the breadth of Kekulé's experimental undertakings.

The most important experimental work to come from a student in Kekulé's private laboratory at Heidelberg was Baeyer's paper on the constitution of cacodyl compounds.[32] In this communication Baeyer demonstrated that the addition of chlorine to cacodyl chloride (dimethyl arsenic chloride) was analogous to the addition of chlorine to ammonia. The resulting addition product was easily decomposed with mild heat yielding methyl chloride and monomethyl arsenic dichloride. In Baeyer's paper, as in Kekulé's on the fulminate of mercury, the formulas for the cacodyls were written in a schematic way designed to indicate the type.

A rather revealing aspect of Baeyer's paper was his observation that, whereas Dumas' plan to designate organic compounds according to mechanical type, based on similar genetic series, had not been widely accepted, the constitution of certain organic substances had in fact, he believed, already been elucidated by the drawing of mechanical analogies in reactions where the disruption of the substance was accomplished by a replacement of one element with an element of another kind. The example which Baeyer cited was Frankland's work on zinc ethyl where he compared the binding of metal and oxygen to that of ethyl and oxygen, specifically calling attention to the fact that the ethyl was analogous to hydrogen and not to oxygen. The difficulties vanish, Baeyer contended, "if the right atomic weight of oxygen is taken, and if the formulas, which contain an odd number of atoms of the same, are doubled." We know that one of the most pressing chemical problems in the 1850's was connected with the search for unambiguous values of the saturation capacity, atomicity, or valency of the elements. Frankland's experiments (1850–54)[33] with the metal alkyls provided a basic solution to that problem, at least for a limited group of organometallic compounds. The reference to the zinc alkyls in Baeyer's paper indicates that precisely those Frankland papers were well known in Kekulé's laboratory which Frankland later mentioned in connection with his own claims as discoverer of the valence theory.

This completes our discussion of Kekulé's experimental activities relative to the question of his valence theory up until and including the year of his fundamental theoretical paper on the quadrivalency and self-linking characteristics of carbon in 1858. We have seen that he had carried out publishable experimental investigations in Will's laboratory in Giessen on amylsulfuric acid (1850), in Von Planta's private laboratory in Switzerland on volatile alkaloids and mineral analyses (1853/54), in Stenhouse's laboratory at St. Bartholomew's Hospital in London on thiacetic acid (1854), and finally as a *Dozent* in his own privately arranged and financed laboratory at Heidelberg on fulminate of mercury, glycolic acid from acetic acid, saccharification of the liver and the so-called amyloids of the spleen (1857/58). This is not an unimpressive record for a young man of age 29.

It remains to be shown how Kekulé manipulated his own experimental results and those of others to formulate an explicit and general valence theory for organic compounds based upon the assumption of a quadrivalent and self-linking carbon atom. It is beyond the scope of this paper to present that aspect of Kekulé's contribution, since it would entail a careful analysis of his two theoretical papers of 1857 and 1858. Much of what Kekulé had to say in those papers had already been implied in the early experimental papers which we have discussed above. To spell out the detailed implications of Kekulé's more mature treatment of the theory would constitute a further investigation into the developmental history of the modern valence theory.

[32] BAEYER, A. VON, "Ueber die organischen Arsenverbindungen," *Ann.*, **105**, 265–76 (1858).

[33] FRANKLAND, E., *J. Chem. Soc.*, **2**, 263–96 and 297–99 (1850); **3**, 30–52 and 322–47 (1851); **6**, 57–71 (1854).

The International Yard and Pound

To secure identical values for each of these units in precise measurements for science and technology, it has been agreed to adopt an international yard and an international pound having the following definition: The international yard equals 0.9144 metre;
The international pound equals 0.45359237 kilogramme.
The international inch, derived from the international yard, is exactly equal to 25.4 millimeters.

The values of the pounds currently in use in the United States, United Kingdom, and Canada are as follows: 1 U.S. pound = 0.4535924277 kilogram
1 British pound = 0.453592338 kilogram
1 Canadian pound = 0.45359243 kilogram
1 International pound = 0.45359237 kilogram

The conversion factor for the international pound was selected so as to be exactly divisible by 7 to give the following value for the grain: 1 International grain = .06479891 gram.

The grain is the common unit in avoirdupois, apothecary, and troy pounds. There are 7000 grains in the avoirdupois pound, and 5760 grains in both apothecary pound and troy pound.

The standard U.S. gallon and the Imperial gallon are so substantially different that a compromise international gallon was not practicable. The U.S. gallon is defined as equal to 231 cubic inches. On the other hand the Imperial gallon is defined as the volume of 10 pounds of water under specified standard conditions. A fairly exact relationship is 1 Imperial gallon = 1.20094 U.S. gallons, or less exactly, 1 Imperial gallon = 6/5 U.S. gallons.

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Contributions of Butlerov to the Development of Structural Theory

The basic theory enunciated by Kekulé and Couper in 1858 made possible all the modern developments of structural organic chemistry, but neither Kekulé nor Couper at first went beyond a bare theortical statement or attempted to make any practical applications. Nevertheless, almost as soon as the theory was announced, one investigator realized its full significance and began to think in essentially modern terms. Alexander Mikhailovich Butlerov (*1*), on the basis of the doctrine of the tetravalence of carbon, was able to establish the principles upon which organic chemistry made its greatest advances. He coined the term "chemical structure," recognized the existence of structural isomers and the number of theoretically possible isomers for a given empirical formula, explained tautomerism, and used the theory as a guide in the synthesis of new and important classes of compounds. All of this was accomplished in the early years of the 1860's, while most other chemists were still trying to free themselves from the confusion of the various type theories.

However, the implications of the structural theory soon began to impress many younger organic chemists, and they too began to use structural ideas, often without realizing that such ideas had already been expressed. Butlerov was keenly aware of his priority in this field, and when he was directly challenged, he did not hesitate to state his claims. Toward the end of the decade, a rather bitter controversy over the question of priority took place between Butlerov and Lothar Meyer. The bitterness was perhaps intensified by a certain spirit of nationalism which is apparent behind the immediate statements of the participants. The Russian school of chemists tended to feel that western scientists neglected their work, while the Germans were not inclined to undervalue the work of their compatriots. It is worth noting, however, that Kekulé himself took no part in the controversy, and Butlerov only entered it when he felt directly attacked, and then his statements were calm and well reasoned. A survey of this controversy casts much light on the early development of the structural theory.

Butlerov had been appointed professor of chemistry at the University of Kazan in 1854, but he had not carried out any important original work during his first years in the chair. In 1857 he was sent abroad for a year of study in Germany and France. During this critical period, in which Kekulé and Couper were developing their theories and preparing them for publication, Butlerov made the personal acquaintance of both men. He made a lengthy visit to Heidelberg during which he developed a lasting friendship for Kekulé, and he studied for five months in the laboratory of Wurtz in Paris, where Couper was also working. There is no doubt that during this year he became well acquainted with the theory of "the chemical nature of carbon."

When he returned to Kazan in August, 1858, he had already begun to develop his ideas on structure. The basic starting point of his thought was that for any given structural formula there existed only one compound, and for any individual compound only one formula could be written. He discarded the idea of Gerhardt who had said that the formula for a compound should vary according to its different methods of synthesis or reaction. Thus Butlerov discarded the type theory altogether. Kekulé continued to use type formulas in his textbook for several years.

By 1861, Butlerov's formulation was so clear to himself that he felt able to present it to western chemists. He read a paper to a meeting of German naturalists at Speyer on September 19, 1861 (*2*) in which he first used the term "chemical structure."[1] His definition was as follows:

> Starting from the assumption that each chemical atom possesses only a definite and limited amount of chemical force (affinity) with which it takes part in forming a compound, I might call this chemical arrangement, or the type and manner of the mutual binding of the atoms in a compound substance by the name of "chemical structure" (*4*).

When Butlerov returned to Kazan, he made a report to the University Senate in which he summed up his impressions of chemical theory in western Europe.

> None of the ideas which I found in western Europe seemed especially new to me. Laying aside here misplaced false modesty, I can say that these ideas and conclusions have been quite familiar in recent years in the Kazan laboratory and they have not been considered especially original; they were part of the general chemical inheritance and some were introduced into the lectures (*5*).

Butlerov now began to contribute a number of papers on aliphatic hydrocarbons and alcohols to western chemical journals. In these he showed that on the basis of structural theory it was possible to predict the number of isomers of various homologous hydrocarbons. His exposition was essentially that used at present in introducing the concept of isomerism in elementary organic chemistry courses.

Other chemists, with increasing frequency, gradually began to use similar structural formulas without realizing that Butlerov had preceded them. At length, in

Presented as part of the Kekulé-Couper Centennial Symposium on the Development of Theoretical Organic Chemistry before the Division of History of Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

[1] Menshutkin (*3*) has pointed out that this term was actually first applied by Lomonosov in 1760, but this usage did not become generally known.

1867, he felt that he must assert his claims to priority. He appended a footnote to his discussion of the number of isomers of C_4H_{10} theoretically possible (*6*), in which he said:

. . .I have given the theoretically possible structures of the hydrocarbons C_5H_{12}. One of these, $C(CH_3)_4$, is completely analogous to the case of $C(CH_3)_2(C_2H_5)_2$; a hydrocarbon which has this latter structure was recently discovered by Friedel and Ladenburg. It is clear that if once the formula $C(CH_3)_4$ is given, so must also the structural case $C(CH_3)_2(C_2H_5)_2$ be foreseen. It appears, however, that Friedel and Ladenburg have neglected the fact that the view which they have newly expressed is entirely analogous to that already given by me much earlier. I must expressly mention that in the chemical literature of recent years such ideas as those I have already published are presented as new and original (without citation).

He then indicated that many chemists, including Lothar Meyer, had made unjustified claims, and concluded,

The estimation of the mutual chemical method of binding elementary atoms in molecules (the principle of chemical structure) will more and more be the chief basis of most chemical speculations in the newer chemistry; of the need for this estimation I have already spoken, and I am now obliged to assert that to me belongs an important part of the priority for complete and consequential development of this principle. This assertion of mine, as I hope, will be found to be solidly based, if one will make a closer acquaintance with my publications which have appeared since 1861.

The mention of Lothar Meyer resulted from a paper which the latter chemist had published in 1866 (*7*) in which he discussed the presence of "unsaturated affinities" (double bonds) in ethylene chloride as follows:

Without the assumption of unsaturated affinities, the constitution of both compounds would be identical, namely: HHCCHCl; with the other assumption there are three possible cases:

.HHCCHCl. ..HCCHHCl ..ClCCHHH

where the monovalent atom next to the C atom is held by this atom and the unsaturated affinity is expressed by a dot.

It can be seen that Meyer was actually using a structural formula in these cases, and he apparently felt that Butlerov was aiming a personal attack at him. He therefore published a bitter counterattack at his assumed foe, which he entitled "To the Defense" (*8*).

In setting up this formula I have neither intended nor believed that I was establishing a claim to priority. Nor does such a right in the least belong to Prof. Butlerov. This and a thousand other formulas are the obvious consequence of the two propositions that carbon is a tetravalent element and that its atoms and all other elements in its compounds are arranged in chains. Both propositions are a part of the rich heritage developed through the tireless work of numerous investigators of organic chemistry. But the first of these propositions was clearly recognized and expressed first and only by A. Kekulé in 1857. The discovery of the second proposition Kekulé divided with A. S. Couper. Kekulé, however, combined these propositions long before Prof. Butlerov, who learned of the chain formation from Kekulé and suggested calling it structure. The establishment of these formulas, carried out through a long series of combinations, permutations, and calculus of variables, required in concrete cases neither unusual genius nor great gifts of discovery. Whether one chemist should express schematically the series of signs which expressed the order of atoms from left to right, as is usual in Europe, or like the Hebrew, from right to left, or like the Chinese, from above down, is merely a matter of taste. Whoever by writing down formulas of this type intends to establish a property right deceives himself. . .he claims things as his newly discovered property which are the common goods of science through the services of others years before.

It can here be seen that Meyer completely misinterpreted the real significance of Butlerov's contributions, reading them as a mere manipulation of symbols and that he committed the very common error of claiming that because a given point of view was becoming obvious to everyone, the man who first realized the meaning of this point of view deserved no credit.

Butlerov was not slow to accept this new challenge. At the time he was making a third trip to western Europe, largely for the purpose of defending his claims, and he was at this time in Nice. From there he sent his reply, which he entitled simply "An Answer" (*9*).

I always was and still am far from misunderstanding the brilliant services of Kekulé in the theoretical and practical branches of our science. I hold, like Herr Meyer, that the idea of chemical structure is a consequence of the recognition of the valence of elements and especially the proposition first recognized and expressed by Kekulé that carbon is tetravalent. I also believe that the idea of chain formation by atoms cannot be neglected. Also I believe that the views expressed by Couper (unfortunately only briefly) are almost identical with those generally accepted and that the formulas given by Couper are actually rational formulas in the present sense of the word, that is, constitutional formulas or formulas of chemical structure.

But what Herr Meyer says about the development and expanded use of these new propositions will, as I believe not be accepted completely by an impartial man.

Aside from the recognition of the new propositions, we still find for several years longer much which had either become superfluous or did not agree with these propositions. This includes the use of types, both compound and mixed, the old way of determining formulas by reaction only, so that for one and the same substance several rational formulas could be given, etc. Similarly, assumptions which did not entirely agree with the new principles were not entirely absent from the writings of Kekulé even *after* I expressed my views on chemical structure and made them the basis for the chief principles of my theoretical speculations. . . . I place no value on the outward appearance of formulas.

After a challenge to Meyer to reread his various papers, Butlerov concluded that he would not "shrink my contribution to developing the new principles to the mere name 'chemical structure' and the use of a certain way of writing formulas."

This reply seems to have ended the polemical part of the battle. It is probable that Butlerov's acknowledgment of the importance of Kekulé's work silenced the German critics. At the same time he stated his own contribution so clearly that it could scarcely be denied. Instead, another fate overtook it. It became so much a part of the basic framework of organic chemistry that it was taken for granted, and the work of the originator was forgotten. This is usually the fate of those who make the initial steps in what later becomes a whole new science in itself.

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The Unraveling of Geometric Isomerism and Tautomerism

Geometric Isomerism

After he had introduced the concept of the tetrahedral carbon atom and used it to explain the optical isomerism of the tartaric acids, malic acid, sugars, camphor, and other compounds, Van't Hoff turned to another type of isomerism which appeared to be a consequence of the tetrahedral atom, namely, "*The influence of the new hypothesis upon compounds containing doubly linked carbon atoms.* Double linking is represented by two tetrahedrons with one edge in common. . ." (*1*).[1]

Van't Hoff pointed out that when two tetrahedrons are joined on an edge (Fig. 1) and the four points carry

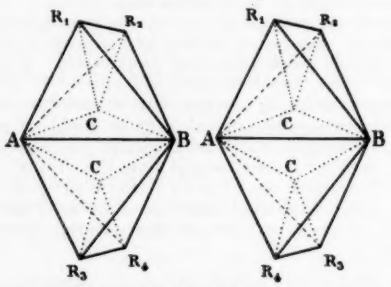
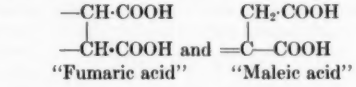


Fig. 1. Isomers possible by joining the edges of tetrahedra (after Van't Hoff).

univalent groups, R_1, R_2, R_3, and R_4, possibilities for isomerism occur when R_1 differs from R_2 and R_3 differs from R_4. This does not preclude an identity of, for example, R_1 and R_3 and R_2 and R_4.

Van't Hoff then called attention to several instances of isomerism where the structures had not been properly resolved, but which were amenable to his interpretation. Let us look at the case of fumaric and maleic acids, his first example.

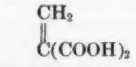
Malic acid was isolated from apple juice by Scheele in 1785. Dry distillation of this acid led to the discovery, in 1817, of fumaric and maleic acids by Braconnot and independently by Vauquelin. Studies by Pelouze in 1836 pointed toward the isomerism of the two acids although the state of organic formulation at this date was too chaotic for certainty on this matter. Liebig in 1838 also obtained the same composition for the two acids but considered the higher melting fumaric acid to be a polymer of maleic acid. Erlenmeyer put forth this explanation in 1870 and again in 1886. Kekulé (*3*) succeeded in reducing both acids to succinic acid in 1861. Later, when attempting to write structures for such isomers, some chemists were inclined to assume the presence of a bivalent carbon atom, as in the case of carbon monoxide. Kekulé, however, was firmly committed to the quadrivalency of the carbon atom and considered the only really appropriate structures to be,



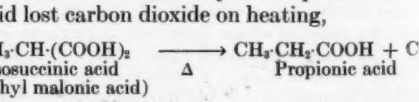
The problem of the structure of maleic and fumaric acids was closely associated with the three isomeric acids, $C_3H_4(COOH)_2$, produced from citric acid by pyrolysis. These acids, named itaconic, citraconic, and mesaconic, were first encountered by Lassaigne (*4*) in 1822 and were extensively studied in Kekulé's laboratory by Swarts (*5*). These investigators postulated four possible structures, each with the carboxyl groups at the ends of straight carbon chains and with two unattached valence bonds on one or two of the central carbon atoms. Kekulé and Swarts believed that such structures were consistent with the properties, but in the second paper they arrived at a genuine double bond in an alternative structure for mesaconic acid when explaining the conversion of itaconic and citraconic acids to mesaconic acid by hydrobromic acid. An analogy to fumaric acid led to the formulas,

which were popular for several years.

Still another formula for maleic acid was introduced by Richter (*6*).



Kekulé rejected this since it was inconsistent in properties with other compounds where two carboxyl groups were present on the same carbon atom. Maleic acid lost water on heating, being converted into an anhydride, whereas such dicarboxylic compounds as isosuccinic acid lost carbon dioxide on heating,



Maleic acid with the Richter formula should therefore decompose to acrylic acid.

Presented as part of the Kekulé-Couper Centennial Symposium on the Development of Theoretical Organic Chemistry before the Division of History of Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

[1] This Dutch publication (*1*), carrying Van't Hoff's paper in French, appeared in September, two months before Le Bel's paper on the same subject in *Bull. soc. chim.*, **22**, 337–47 (1874). Van't Hoff's paper was published in enlarged French translation in 1875 under the title, "La chimie dans l'espace." Both papers are found in English translation in Richardson (*2*). Quotation from the latter, p. 42.

$$CH_2{=}C(COOH)_2 \xrightarrow[\Delta]{} CH_2{=}CH{\cdot}COOH + CO_2$$

Furthermore, on hydrogenation it should yield isosuccinic acid rather than succinic acid.

$$CH_2{=}C(COOH)_2 \xrightarrow{H_2} \underset{\text{Presumed}}{CH_3{\cdot}CH{\cdot}(COOH)_2} \quad \underset{\text{Observed}}{[HOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOH]}$$

Van't Hoff recognized that the dilemma might be easily resolved by the application of his principle involving the joining of two tetrahedral carbon atoms on an edge. This gave the structures,

He saw signs of similar isomerism in such pairs as brommaleic acid and iso-brommaleic acid, citraconic and mesaconic (methylmaleic and methylfumaric) acids, and liquid and solid crotonic acids.

Solid crotonic acid was discovered in the seeds of *Croton tiglum* by Pelletier and Caventou (*7*), and isolated from croton oil by Schlippe (*8*). Will and Körner (*9*) prepared the acid synthetically from allyl cyanide. As a result of this synthesis the formula was considered to be

$$CH_2{=}CH{\cdot}CH_2{\cdot}COOH \qquad (1)$$

A decade later Kekulé (*10*) found that crotonaldehyde was formed during the condensation of acetaldehyde. He went on to show that the formula of the solid crotonic acid formed therefrom by air oxidation had the formula,

$$CH_3{-}CH{=}CH{\cdot}COOH \qquad (2)$$

and showed that crotonic acid formed from allyl cyanide also had formula (2), as the result of the migration of the double bond during synthesis. However, a liquid crotonic acid was known and the assumption was made that this had formula (1) (*11*).

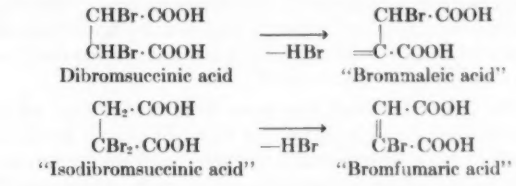
Van't Hoff argued that it was more logical to assume that the liquid and solid crotonic acids both had formula (2) since they both gave almost quantitative yields of acetic acid upon fusion with KOH, both gave acetic and oxalic acid on oxidation, and the liquid acid isomerized to the solid acid on heating at 170–180°C. He felt that the isomerism that existed was similar to that found in maleic and fumaric acids. The correctness of his reasoning was shown later when vinylacetic acid was synthesized and found to have structure (1) (*12*). Van't Hoff included in this same class the chlorocrotonic and chloroisocrotonic acids prepared by Geuther (*13*).

The papers of Van't Hoff and Le Bel were received with a good deal of skepticism and since Van't Hoff's was more imaginative and broader in its scope he naturally came in for the bulk of the criticism. Le Bel had introduced the concept of the asymmetric carbon atom but had not gone on to suggest a geometry of the atom. Van't Hoff had, on the other hand, directed the four valences of the carbon atom toward the corners of a tetrahedron and used the tetrahedron freely in his explanations. He had also dealt with the nature of double and triple bonding which Le Bel had overlooked in his original treatment of the subject.

Kolbe, in typically cantankerous fashion, castigated Van't Hoff as an example of the backward trend in German chemical research, the regeneration of the discredited *Naturphilosophie* which had stood discredited for fifty years as the result of investigations in exact science. He dismissed the work with (*14*):

> A Dr. J. H. van't Hoff, of the veterinary school at Utrecht, finds as it seems, no taste for exact chemical investigation. He has thought it more convenient to mount Pegasus (obviously loaned by the veterinary school) and to proclaim in his "La chimie dans l'espace" how during his bold flight to the top of the chemical Parnassus, the atoms appeared to him to have grouped themselves throughout universal space.

Fittig opposed the Van't Hoff proposals for fumaric and maleic acids, preferring to use the Kekulé formulas. Fittig and his students (*15*) studied the removal of hydrogen bromide from the two isomeric dibromsuccinic acids and postulated the following changes:

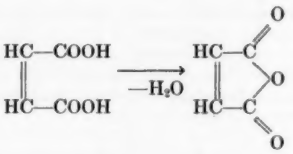


Claus (*16*), Lossen (*17*), and Hinricksen (*18*) were among those who criticized the theory on the basis of incompatibility with physical laws (*19*). The physical science of the time was not prepared for a concept in which the forces of the atom were oriented in several different directions.

There were, however, certain organic chemists who overlooked the alleged taint with *Naturphilosophie* and the incompatibility with physical theory to apply the concepts to the practical problems of structural organic chemistry facing them at the time. There were numerous cases of structurally unexplained isomerism to which the new concepts were applicable. Johannes Wislicenus was clearly the leader in recognizing the value of the new theory. Soon after seeing the French version of Van't Hoff's book he wrote enthusiastically to the author urging translation of the work into German. Felix Hermann, one of Wislicenus' students, undertook the translation which was published in 1877 as "Die Lagerung der Atome im Raume," with a preface by Wislicenus.

Wislicenus was active, during the next two decades, in the pursuit of structural problems. It was partly his early work with lactic acid which had led Van't Hoff to recognize the nature of the asymmetry of optically active carbon compounds. Now Wislicenus proceeded, through the application of Van't Hoff's theoretical constructs, to work out the structure of a variety of compounds. A large part of his work dealt with optical isomerism but his work with the isomers of monochloropropylene, bromobutylene, dibromobutylene, chlorocrotonic acid, and the maleic-fumaric acid pair represented significant pioneering with the new concept of geometric isomerism (*20*). At the same time a number of other workers, notably Fittig, Erlenmeyer, Michael, Beilstein, and Anschütz, were attempting to solve structural problems without use of the new concepts. After a succession of failures some of these workers slowly came to accept the new viewpoint (*21*).

The correct selection of *cis* or *trans* configuration for individual isomers was seldom an easy matter and in certain cases could not be made for many years. In the case of maleic and fumaric acids the *cis* form was assigned to maleic acid by Van't Hoff because of the ease with which the anhydride was formed upon warming the acid.



Of course this was not clear proof since it was known that isomerization took place under a variety of conditions, particularly in the presence of halogens and halogen acids. Fumaric acid gave the same anhydride but much more slowly and at higher temperatures. Studies on the cold water hydrolysis of maleic anhydride formed from either maleic or fumaric acids always resulted in the formation of maleic acid.

The research which had been done on the two acids was subjected to a lengthy and critical analysis by Wislicenus (*22*) who concluded that the *cis* form for maleic and the *trans* form for fumaric acid were most consistent with the facts. This was based very largely on the addition reactions of the two unsaturated acids and on the rearrangements brought about by the halogens and hydrohalogen acids. Ossipoff (*23*), Anschütz (*24*), Petri (*25*), and Kekulé had made such studies with the finding that maleic esters were readily converted into the more stable fumarate form.

Kekulé (*26*) and Anschütz (*27*) showed that the oxidation of maleic with alkaline permanganate resulted in the formation of *meso* tartaric acid whereas the oxidation of fumaric acid gave the racemic mixture of *dl*-tartaric acids. Wislicenus (*28a*), assuming that no rearrangement took place during the permanganate oxidation, argued that the opening of the double bond of maleic acid would result in formation of the internally compensating form of tartaric acid regardless of which bond was opened (see Fig. 2).[2] With fumaric acid, however, the opening of one bond (2,2′) would give *d*-tartaric acid, the other (1,1′) would give *l*-tartaric acid (see Fig. 3). Wislicenus went on to suggest that the characteristics of the dibromosuccinic acids formed on bromination of maleic and fumaric acids must be entirely analogous. While these acids had been prepared in Kekulé's laboratory their optical behavior was not clearly established. In 1925 Terry and Eichelberger (*29*) showed that *cis* addition is not characteristic of bromination, maleic acid yielding *dl*-dibromosuccinic acid, fumaric acid the *meso* form.

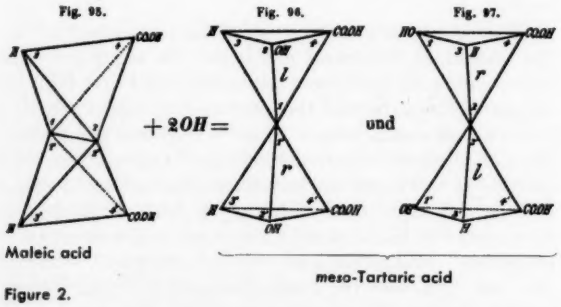


Figure 2.

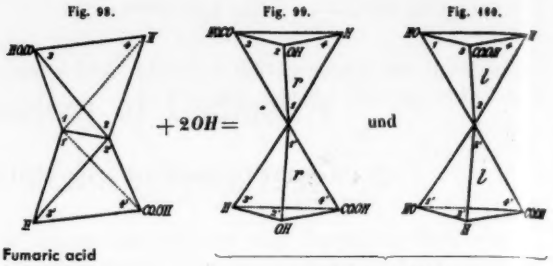


Figure 3.

Wislicenus was aware of the influence of halogens and hydrohalogen acids in the conversion of maleic into fumaric acid. There were also cases where one acid was converted into a derivative of the other. In extensive researches Wislicenus (*28b*) showed that, following halogenation, quantities of hydrohalogen acids became detectable in the reaction mixture. This led him to suggest a mechanism in which halogenation was followed by rotation to a "most favored position" and splitting out of a hydrohalogen molecule (*28c*). Thus, for maleic acid ("Fig. 78") bromination produced dibromosuccinic acid ("Fig. 79") which then rotated to the "most favored position" ("Fig. 80"), after which hydrogen bromide split out to give bromofumaric acid ("Fig. 81").

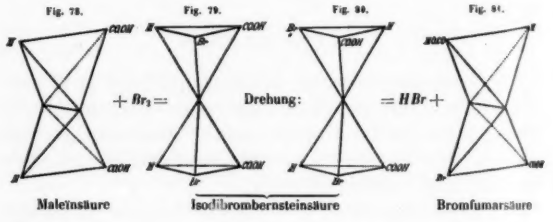


Figure 4.

In a similar manner he explained the formation of bromomaleic acid from fumaric acid in the presence of bromine ("Figs. 74–77"). By analogous reasoning he showed that in the presence of hydrobromic acid, maleic acid would be converted into fumaric acid, whereas fumaric acid would remain unconverted. This was in accord with experimental observations.

Wislicenus went on to apply his reasoning to other cases of geometric isomerism. For the three pyrolysis products of citric acid he showed that itaconic acid could

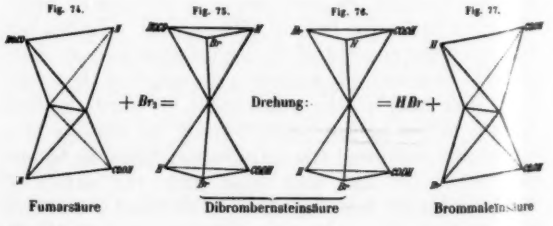
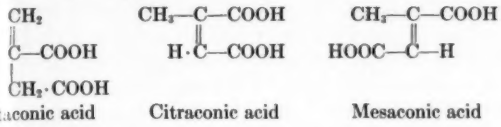


Figure 5.

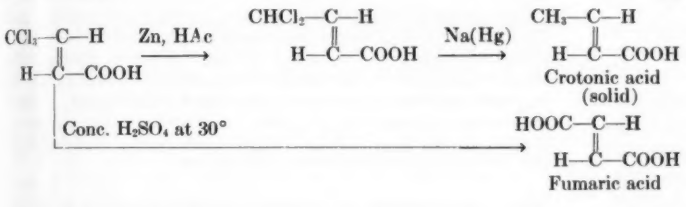
[2] Figures 2–5 are from Wislicenus' paper (*20*).

show no geometric isomerism and was assigned the formula below. Citraconic acid, because of its easy convertibility into mesaconic acid by hydrobromic acid was assigned the *cis* form.



Although Wislicenus attempted to deal with the isomerism of solid crotonic and liquid crotonic acids he was unable to relate them to an unambiguous reference compound, and his analysis of their reactions led him to assign the *cis* form to solid crotonic acid.

The correct orientation of the crotonic acids was not finally established until 1923 when Von Auwers (*30*) was able to relate the solid acid to fumaric acid by preparation of each acid from a common substance under conditions where rearrangement around the double bond was unlikely.



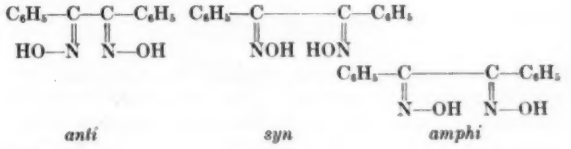
Cinnamic acid shows the same relationship, the higher-melting natural form having the *trans* configuration. Here again Wislicenus attempted to deal with the orientation but confessed inability to make a decision with certainty. He tentatively but erroneously decided in favor of the *cis* form for the natural acid.

Following the pioneering work of Wislicenus there has been continued progress in establishing the geometric structure of unsaturated compounds although the problem is frequently fraught with danger when superficial studies are made. Greatest confidence can be had in those cases where the *cis* isomer can be related to a compound of unquestionable structure through ring closure or ring opening. After the structure of a number of isomers was clearly established, physical properties were found to vary in a definite manner between isomers and this has become a useful tool, at least for indicative value. Melting points were found to be lower for *cis* isomers, while solubility in inert solvents, dissociation constants (of acids), and heats of combustion were found lowest for *trans* isomers (*31*). Debye (*32*) established the configuration of the two dichloroethylenes by measuring the distance between chlorine atoms from X-ray diffraction patterns. In the lower melting isomer, which had been termed *cis*, the distance was 3.6 Å whereas in the other isomer the distance was 4.1 Å. Other physical properties have been utilized with some success.

The geometric isomerism of nitrogen compounds was recognized about 1890. Goldschmidt (*33*) observed two isomeric benzildioximes ($C_6H_5C{:}NOH)_2$, as early as 1883. Victor Meyer and Von Auwers (*34*) verified the isomerism of these two compounds and discovered a third isomer. They sought to explain the isomerism by postulating restricted rotation between two of the carbon atoms. About this time Beckmann (*35*) prepared an isomer of benzaldoxime, $C_6H_5CH{:}NOH$, which he considered to be a structural isomer. Goldschmidt (*36*), however, established the general structural identity of the two isomers as oximes.

In 1890, Hantzsch and Werner (*37*) pointed out that if the three valences of nitrogen did not lie in the same plane, the oximes might be expected to show a *cis-trans* type of isomerism. Thus, the two benzaldoximes were formulated as

and the three benzildioximes as



This type of reasoning was found consistent with the experimental knowledge of the known aldoximes, ketoximes, dioximes, oximido acids, hydrazones, and related compounds, although some problems were encountered with such oximes as were involved in tautomeric phenomena.

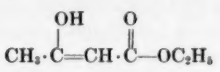
Once the tetrahedral character of the nitrogen valences was established it was apparent that geometric isomerism should be observed not only in those compounds with a carbon to nitrogen double bond but also in those with a nitrogen to nitrogen double bond. Isomeric diazo compounds, which began to be reported during the nineties, were at first interpreted by their discoverers as structural isomers. It was largely through the work of Arthur Hantzsch at Leipzig that the matter was clarified as another instance of geometric isomerism (*38*).

Tautomerism

During the 1860's and 1870's various pieces of evidence were accumulating which suggested that certain compounds had properties which were consistent with more than one formula. This was the case with Kekulé's explanation of the failure to observe two *ortho*-disubstituted benzenes, but it was even more striking in the case of certain other compounds. The compound of greatest interest was acetoacetic ester but there were enough other examples to show that the phenomenon was not unique to this compound.

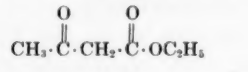
Acetoacetic ester was first prepared in 1863 by Geuther (*39*) who believed that acetic acid contained replaceable hydrogen atoms and attempted to prepare a sodium salt of ethyl acetate by reaction with metallic sodium. The evolution of hydrogen was observed along with the formation of a crystalline compound having the formula, $C_6H_9O_3Na$. It was learned that ethyl alcohol needed to be present in the reaction mixture so that sodium ethoxide, which served as a catalyst, would be formed. Acidification of the crystalline compound gave a liquid which was neutral to litmus but reacted with bases to form salts. The sodium salt with ethyl

iodide gave an ethyl derivative. The compound was named ethyl diacetic ester and was formulated as,



The nature of the reactions involved was not clearly understood until the work of Wislicenus (*40*) more than a decade later.

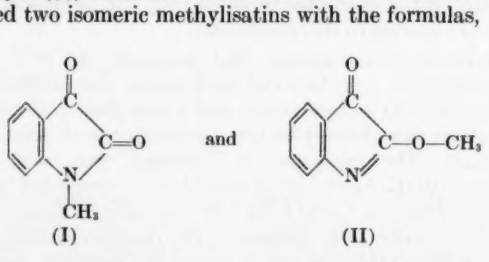
Shortly following Geuther's original work the same compound was prepared by Frankland and Duppa (*41*). In contrast to Geuther, they observed the ketonic character of the compound and named it acetone carboxylic ester which came to be formulated as



Various investigators who studied the compound reported variant properties. The structural formulas proposed for the ester emphasized the presence of unsaturation and an active hydroxyl group on the one hand, ketonic character on the other. Through the work of Claisen, this and similar compounds came to have great usefulness in organic syntheses.

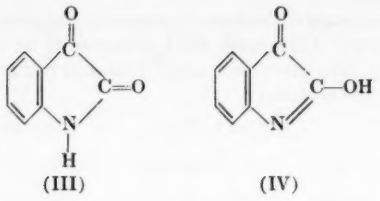
Butlerov (*42*) prepared two isomeric di-isobutylenes in 1877 by the action of sulfuric acid on trimethyl carbinol. He assumed the formation of these isomers on the assumption of an equilibrium between the two hydrocarbons, water, and the corresponding alcohols. Butlerov suggested the existence of such isomerism even in the absence of a reagent. "In these cases in every investigation concerning the chemical structure of the substance, the molecule will always behave in two or more isomeric forms. It is clear that the chemical reactions of such a substance must occur in accordance sometimes with one and sometimes with the other chemical structure, depending on the reagent and on the experimental conditions." He used as examples the cases of cyanic and prussic acids, the former suggesting an equilibrium mixture of carbimide and cyanogen hydroxide, the latter a mixture of the nitrile and isonitrile. These speculations were to ultimately receive experimental support (*42a*).

When Erlenmeyer (*43*) in 1878 attempted to isolate alcohols with the hydroxyl group directly attached to double-bonded carbon by treatment of appropriate halogen derivatives with metal hydroxides he obtained in every case the isomeric carbonyl compound, and concluded that alcohols of this type undergo conversion into carbonyl compounds at the moment of formation. Baeyer (*44*) encountered similar difficulties when he isolated two isomeric methylisatins with the formulas,



(I) (II)

These supposedly came from the same parent compound (IV) since he was unable to isolate the equivalent of formula (III) which would be expected to be



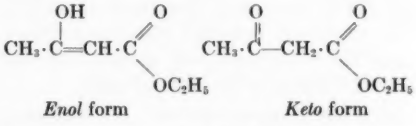
(III) (IV)

the precursor of (I).

The name *tautomerism* (Gr., *tauto*, the same) was introduced for such cases by Conrad Laar (*45*) when he discussed the phenomenon in 1885. He pointed out that one substance could combine the properties of two isomers, giving as examples, isatin, ethyl acetoacetate, and the identity of *para*-nitrosophenol and quinone monoxime, and of benzeneazo-alpha-naphthol and alpha-naphthaquinonephenylhydrazone. He postulated a change in the position of a hydrogen atom, resulting in the existence of two structures in equilibrium with one another. As Schorlemmer remarked a few years later (*46*),

> The atoms within the molecule are in continual motion, and thus one form of a compound changes into another; the light atoms of hydrogen, the comet of the elements, moving the quickest, gets outside the sphere of attraction of a heavier atom, and comes within the sphere of attraction of another one. But if we replace hydrogen by an element or radical, moving more slowly, the latter does not get beyond the sphere of attraction, and the unstable form becomes a stable one.

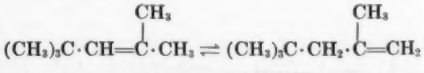
Thus, the formula for acetoacetic ester came to be written in two forms, for which Brühl (*47*) proposed the names *enol* and *keto*.



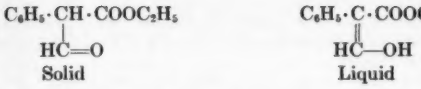
Enol form *Keto* form

P. Jacobson (*48*) objected to the term, *tautomerism*, since he felt that it implied a continuously changing constitution. He preferred to believe that both forms of the compound were present in a stable state with change from one into the other occurring only under the influence of certain reagents. He proposed the term *desmotropy* (Gr., *desmos*, ligament; *tripein*, to change) which suggested a change in atomic linkage. Hantzsch and Hermann (*49*) proposed that both terms be used, *desmotropes* for such compounds as could be isolated in one form or both, *tautomers* for such cases where isolation of a pure structural form was not possible. *Desmotropy* has gradually fallen into disuse with *tautomerism* referring to the dynamic equilibrium of two readily interconvertible isomers.

Butlerov (*42*) was the first to recognize a case of such equilibrium through his preparation and study of the diisobutylenes in 1877. The acid-catalyzed equilibrium was postulated to be

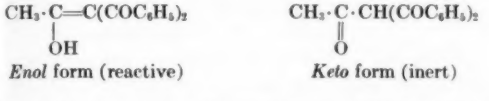


Twenty years later Wilhelm Wislicenus (*50*) isolated two ethyl formlyphenylacetates, a solid unreactive toward ferric chloride and a liquid which gave a color with the iron salt. On standing the solid slowly isomerized to the liquid form



Solid Liquid

About this same time Claisen (*51*) reported results of studies which led to the isolation of dibenzoyl acetone in two solid modifications. While the molecular weights were identical they showed marked differences in their chemical properties, especially toward metallic salts and alkalies. One form exhibited acid properties and with ferric chloride gave an intensely colored salt. The other form exhibited no acidic properties and was indifferent toward ferric chloride. This indifferent form, however, passed into solution upon standing but the salt formed was that of the other modification. Claisen diagnosed the two forms to be the *enol* and *keto* forms in 1896 and suggested the structures,



Enol form (reactive) *Keto* form (inert)

Hantzsch (*52*) isolated two isomers of phenylnitromethane, a solid form with acidic character and a neutral liquid. Claisen and others obtained similar results with other compounds. In some cases at least two pure solid substances in *keto* and *enol* form were shown to be capable of passing into each other without a reagent being present. An equilibrium mixture was formed. If a reagent capable of reacting with one form was added the reactive form was constantly regenerated from the non-reactive form until the reaction is complete. The cases studied by Claisen were all slow-reacting which made it possible to observe what was happening. Claisen never recognized the reversibility of the change because he never obtained his *keto* form in pure state. W. Dieckmann (*52a*) later demonstrated this fact and proved the interconvertibility.

At an earlier point W. Wislicenus and L. Knorr recognized the reversibility of the change. Wislicenus obtained a liquid *enol* and a crystalline *keto* form of a certain compound and showed that the equilibrium mixture could be obtained from either direction.

In 1911 Knorr (*53*), and independently, K. H. Meyer (*54*), succeeded in obtaining ethyl acetoacetate in two modifications. The crystalline *keto* form was obtained by cooling a concentrated solution of the ester in petroleum ether, hexane, or methyl ether at −78°C. The *enol* form was obtained by decomposing a suspension of the sodium compound in petroleum ether with a limited amount of hydrogen chloride at the same low temperature. The *keto* crystals melted at −39°C. They gave no coloration with ferric chloride and remained stable at ordinary temperatures for several days if catalysts were rigidly excluded. Hydrochloric acid, ferric chloride, or even a trace of tobacco smoke caused them to revert to the equilibrium mixture in a few seconds. The *enol* ester gave an immediate intense coloration with ferric chloride but on holding it passed into the same equilibrium mixture as was obtained from the *keto* form.

With the growth of use of electronic structures in explaining organic combination it was natural that electronic mechanisms would be introduced into the explanation of tautomerism. From an analysis of electron affinity J. F. Thorpe, Robert Robinson, and particularly C. K. Ingold deduced the effects of neighboring groups on nearby electrons (*55*). Of course, there have been numerous cases where the existence of separate forms in equilibrium has not been demonstrable, yet a single formula is inadequate to explain the properties of the compound. Here the resonance concept of Pauling (*56*) has been of great value in the interpretation of structure.

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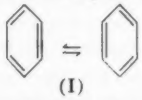
The Contributions of Fritz Arndt to Resonance Theory

Kekulé's ideas on tetravalence and self-linking of carbon atoms, which were so important in the development of structural theory, were described in 1858, just one hundred years ago. Only seven years later, in 1865, Kekulé (*1*) showed how these ideas could explain the composition and anomalous behavior of the "aromatic" substances, by assuming the structure of benzene as a nucleus of six carbon atoms in a ring, with alternating single and double bonds. Kekulé believed, but was unable to prove, that the six combining positions of benzene were identical. The Kekulé structure has been called "the most fruitful single suggestion in the history of organic chemistry"(*2*).

During the next decade, Kekulé's first postulate that the six combining valences of benzene were equivalent was quickly demonstrated by Ladenburg and Wroblewsky and then by Körner, with the first applications of what was later to be called the "absolute" method. Thus within ten years the structure of benzene as a symmetrical hexagon with six equivalent hydrogen atoms was pretty well established. At the same time, a much more difficult problem was presented, that of the actual location and function of the six carbon valences of benzene which are not needed to hold the atoms in place. Kekulé himself soon suggested (*3*) that oscillation occurring between the two possible arrangements of the double bonds (I) would account for the non-existence of certain isomers of disubstituted benzenes, and be more consistent with the apparent lack of unsaturation in aromatic compounds.



(I)

However, the concept of moving bonds in molecules was never quite satisfactory, and several other suggestions to account for the unused carbon valences in a manner consistent with the "aromatic" chemical properties of benzene were put forward. Among these were the Claus *para*-bond formula, II, and the Armstrong-

(II)

(III)

Baeyer centric formula III. Perhaps the best of these suggestions was advanced by Thiele (*4*), and was based on his ideas of partial valence used to explain the α,γ-reactions observed in olefins containing alternating single and double bonds. This he called "conjugation," and he pointed out that in benzene the conjugation was cyclic and endless, and therefore unreactive. This suggestion was valuable in that it related "aromatic" character to the behavior of certain aliphatic compounds, but, like previous suggestions, it depended on unorthodox valence concepts.

Regarding these suggestions, F. G. Arndt states (*5*):

> Kekulé's idea of the oscillating double bonds in benzene was the closest approximation to the resonance interpretation of benzene and similar molecules achieved during all the time from Kekulé up to 1924. I think this is so because Kekulé's idea represented the state of benzene as one in which both Kekulé formulas have equal shares, without altering the valencies as such; whereas all the later theories of Thiele Kauffmann, Werner, Weitz, and others, introduced "partial valencies," "secondary valencies," "free

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valencies," etc., which turned up and disappeared again arbitrarily. All these attempts within the framework of unitarian theory, though useful in detail, were contradictory to the fundamentals of stoichiometry which are based on the *indivisible* units of valence. So Kekulé's idea, and the theories of Thiele, Weitz, and others cannot be regarded as anticipations of the theory of resonance because they missed the main point, namely, the interrelation between valencies and *ionic changes*. In all resonating systems zwitterionic structures are involved, even in the case of benzene where the reaction formulas for aromatic substitution are zwitterionic.

With the development of the electronic theory of valence about 1916, ideas based on the work of Langmuir, Lewis, and others on electrical charges began to be applied to organic molecules. An important idea presented at this time was the suggestion (*6*) regarding the amino-acids as molecules containing separated charges (Zwitterions). However, the problem of the non-bonding valences of benzene was still being considered in terms of unusual partial valence or oscillating valence concepts in the early 1920's (*7*).

In 1924, Fritz Arndt published the first paper containing the "resonance hybrid" idea (*8*), which within the next ten years was firmly established as the proper explanation of aromatic behavior by the molecular orbital calculations of Hückel (1932) and the valence-bond treatment of Pauling and Wheland (1933). In 1934, Ingold (*9*) used the term "mesomerism" meaning "between the parts" for this concept, and this term has been widely adopted to describe modern views of resonance.

Arndt (*8*) dealt with the nature of bonds in pyrone ring systems. It was well known the γ-pyrones (V) did not exhibit the characteristic reactions of olefins or ketones, such as addition of halogens or reaction with phenylhydrazine, etc. Nor does γ-pyrone give the

(IV) (V) (VI) (VII) (VIII)

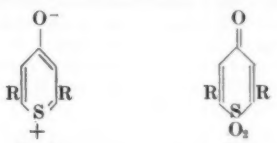
characteristic halochromic reaction of the doubly unsaturated ketones in strong acid. To explain this peculiar "aromatic" character of γ-pyrone, Collie (*10*) had suggested the oxonium oxide formula, VI, containing a tetracovalent ring oxygen atom. In 1924 (*8*) Arndt wrote formulas IV and VII, showing γ-pyrone and γ-thiopyrone as zwitterion dipolar molecules. More important, he clearly recognized that the two formulas, betainic dipoles, IV and VII, on the one hand and unsaturated ketones, V and VIII, on the other, were limiting structures only. He wrote (*11*):

> It is to be emphasized that both formulas, and especially formula VII, represent formulations of extremes; dimethylthiopyrone, as shown by its solubilities, etc., is certainly not such a clear-cut betainic dipole as formula VII would indicate. But with the new views (Zwitterions) according to which no new bond across the ring is involved but all boils down to a shift of electronic orbitals, any intermediate states (Zwischenstufen) can be conceived.

Regarding this publication, Arndt later wrote (*5*):

> You see that in this paper I have, to save space, not inserted the Collie formula, but at once translated it into the zwitterionic formulas IV and VII. Later on I had reason to regret this: some authors got it into their heads that my zwitterionic formula was Collie's. Confronting the Collie formula and formula IV would have better shown the decisive transition from classical unitarian theory to electronic theory. What I had in mind in 1923–24 was this: The objections of earlier authors (WILLSTÄTTER AND PUMMERER, *Ber.*, **38**, 1463 (1905)) to the Collie inner salt idea of the pyrones were due to Collie's misleading formula based on classical onium theory. But a few years before 1924 Pfeiffer had shown that inner salts have to be regarded as zwitterions (see footnote 7 on page 1905).[1] So the Collie formula has to be replaced by formula IV. But this formula, in contrast to the Collie one, shows no bond between the two oxygen atoms, so the objections are no longer valid; and it shows the same order of sequence of all the linked atoms as does the ketonic formula V (or VIII). And in such cases the real state of the system can be regarded as being in between the two formulas; the real intermediate state depends on constitutional factors as shown all over paper 1 (Ref. 8). It should be noted that Sir Robert Robinson, one of the first pioneers of electronic theory, formulated in 1925, i.e., only one year after my first paper, the potential electronic shifts in pyrones and similar systems which would lead from distribution V to distribution IV. In doing so he made a more detailed use of electronic theory than I had at first done; but he did not speak of a definite "intermediate state" of the molecule in between V and IV.
>
> Although the 1924 paper referred experimentally only to pyrones and thiopyrones, the Zwischenstufe theory was quite a general one; but to revert to it in other papers I had to wait for experimental material. During 1924–29 my co-workers, e.g., Eistert and the students who attended my Breslau lectures, heard much more about it. During the 1920's every author of organic papers in Germany had to contend with severe rules of utmost brevity; it happened very often that papers were returned for abbreviation, and any organic theory was frowned upon. So I could express theoretical views only in connection with experimental work, and even then only very shortly. In 1927 I tried to publish a general theoretical paper on the idea of "Zwischenstufe" and "Zwischenzustand" (resonance), but I was told to insert such views in experimental papers.

In 1925, it was shown (*12*) that when the extra electron pairs of the sulfur atom in 1-thio-γ-pyrone (IX)



(IX) (X)

are tied up by oxidation to the sulfone (X), the resonance is no longer possible and the 1-thio-γ-pyrone dioxide shows, in fact, the typical functional group reactions of a diolefinic ketone, in contrast to the behavior of IX. These ideas were applied to nitrogen heterocycles in 1929 (*13*) when in discussing the chemistry of carbostyril (XI) the betaine-bond system XII was

(XI) (XII)

proposed to account for the inactivation of the ring double bond. In 1930, a paper on γ-pyridones appeared (*14*) in which the difference between tautomeric equilibrium and Zwischenstufe was discussed in modern terms of electron resonance. "Formulas VIII and IX" (Keto and Zwitterion formulas of γ-pyridones) "show the

[1] This footnote reads, "Formula IV stands in the same relationship to the Collie formula as the Pfeiffer betaine formula does to the old ring formula of Betaine." Ref. 8, p. 1905, footnote 7.

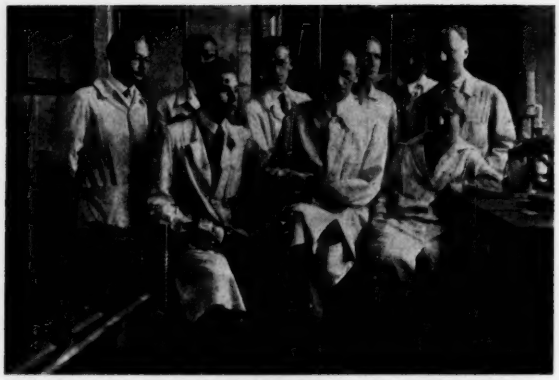


Figure 1. The Breslau Laboratories, 1928. Seated, front, left to right: Amende, Arndt, unidentified. Standing, rear, left to right: Martius, unidentified, Eistert, unidentified, Bakir, Partale.

same position of all atomic nuclei and differ only in the electron orbitals, whose shifts proceed so fast that every pair of formulas represents one single molecule . . ." (*15*). Arndt writes (*5*):

As this paper was partly misunderstood by Von Auwers, I at long last succeeded in getting the general paper (*16*) (on Equilibrium and Intermediate stages) accepted. This paper sums up, I think, the whole theory as far as it could be developed at that time, with no quantum mechanics. To get it published I had to do some bickering with the Editors; the physical chemists among them made me insert the lines on page 2964 about "Verweilzeit" (duration) and "Ubergangzeit" (transition time) and on p. 2965 about "Quantenstufe"; but as I did not want to commit myself so much to the oscillation model of Zwischenstufe I then inserted the lines on page 2965 which I translate: "Whether the limiting states symbolized by the formulas are reached at all (and, therefore, the Zwischenzustand has to be expressed by a time integral of electronic motion) or whether the electronic system remains, even in the strictest sense, always suspended in balance between the limiting states, that is a question which can perhaps be raised and answered from the point of view of quantum and wave mechanics; from the chemical point of view it is irrelevant." As you know, the answer was given three or four years later by the quantum mechanical work of Pauling and Hückel, and rather in favor of the second alternative.

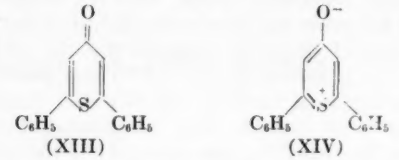
In 1932, similar ideas regarding Zwischenstufe in amide linkages, particularly in the case of cyclic amides, appeared in a paper with Martius (*17*). The subject of mesomerism of the amide group and the aromaticity of cyclic amides appeared in many later papers with Eistert and others.

Regarding the development of the Zwischenzustand theory, Arndt wrote (*5*):

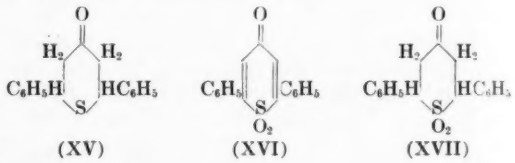
During the years 1924–32 my publications referring to the general chemical theory of Zwischenstufe (resonance hybrid) and Zwischenzustand (resonance) were too scattered and the whole idea too unconventional, to be generally accepted or even universally noticed. It only gained momentum when, in 1933–35 the quantum mechanical work of Pauling, Hückel, and Ingold confirmed it independently and put it on a much sounder physical basis. At that time I was already at Istanbul as a refugee from the Nazi regime. In 1935 Eistert wrote me: "Look here, Meister, your views which I have known for 10 years are now emerging in the theory of resonance; you simply must publish something to connect the two." But as a black sheep in Nazi Germany I could not hope to publish such a paper alone, so Eistert did it together with me. (This paper, entitled "About Resonance and Zwischenstufen Ideas in Organic Substances with Multiple Bonds and Their Electronic Formulas" (*18*) relates the chemical ideas of previous papers to current ideas on resonance, and provides an excellent bibliography of the early work leading to resonance concepts.) A year later the concept of Zwischenzustand or resonance was spoken of and used for a rational mechanism of the Claisen condensation: (in a paper with Eistert (*19*)) on page 2382 both of these terms were replaced by Ingold's term mesomerism, and since then the term Mesomerie has been the current one in German and French literature.

In 1938 the need was felt in Germany for a book elucidating the importance of electronic theory in general and its application to tautomerism and mesomerism. Under normal circumstances, Arndt probably would have been invited to write such a book, but at that time his book publications were forbidden by the Nazis. An excellent review by his former colleague, Eistert (*20*) was published.

Arndt's appreciation of the implications of the Zwischenstufe theory are indicated by the work done while visiting the laboratories of Robinson, after leaving Germany in 1933. In a paper entitled, "Studies on Dielectric Polarisation, XII. Dipole Moments and Structures of Thiopyrones and Related Compounds" (*21*), it was pointed out that 2,6-diphenylthiopyrone cannot exist exclusively either as the ketone (XIII) nor as the betainic dipole (XIV) since the calculated moment for XIII was 1.5 and that of XIV nearly 20, whereas the observed value was 4.4. Moreover, using data of Lorentz obtained at Breslau (*22*) on heats of combustion of XIII, the related saturated compound XV, and their respective sulfones XVI and XVII, it was shown that compound XIII possessed 80−47 = 33 kcal of "resonance" stabilization.



(XIII) (XIV)



(XV) (XVI) (XVII)

Heats of combustion

XIII = 2165 kcal	XV = 2268 kcal
XVI = 2118 kcal	XVII = 2188 kcal
Δ_1 = −47 kcal	Δ_2 = −80 kcal

Fritz Arndt

Fritz Georg Arndt was born in 1885. After receiving the doctorate from Freiburg in 1908, he worked as research assistant to Von Auwers and Gatterman at Freiburg. He was appointed University Assistant at Kiel in 1910, and Lecturer in Chemistry there in 1912. In 1915 Arndt became Professor of Chemistry at the Imperial Ottoman University of Constantinople. Following the Armistice, he returned to Germany in 1918 and was appointed extraordinary Professor of Chemistry at Breslau, being promoted to Professor in 1927 (see Fig. 1). Dismissed by the Nazis in 1933, he was invited to join the Department of Organic Chemistry at Oxford as researcher and guest lecturer. In 1934 he left Oxford to accept the chair of General Chemistry at the University of Istanbul. He was a guest lecturer at a Conference on Organic Sulfur Compounds, held at Indiana University in the summer of 1951, and he was

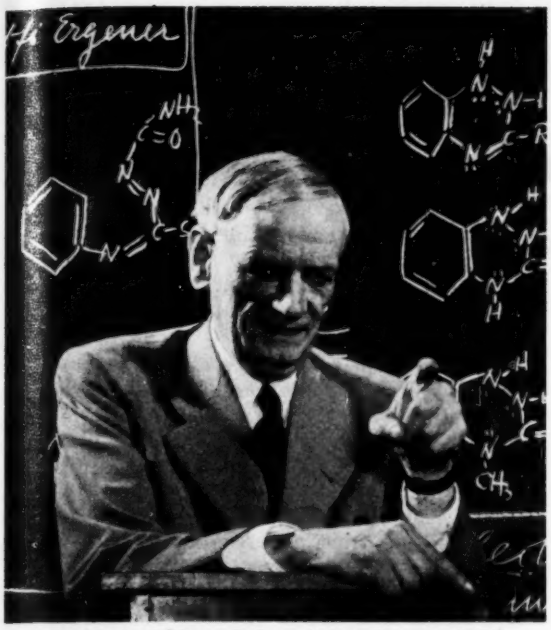


Figure 2. Fritz Arndt (Visiting Professor, Indiana University, 1954).

visiting Professor of Chemistry at Indiana University in the spring of 1954 (see Fig. 2). During this visit to the United States he delivered the Reilly lectures at Notre Dame and the Priestley Lecture at Pennsylvania State University. He retired from the University of Istanbul in 1955, and is now lecturing at Hamburg University as an honorary professor. In the spring of 1957 he circled the globe, giving lectures in Egypt, Australia, and various universities in the United States, on new problems regarding resonance in unusual heterocycles.

His continued interest in problems of resonance and mesomerism is illustrated by the great number of his later papers in which research was undertaken to provide evidence for the correctness of the theory, including its more modern refinements, one of the most recent appearing in 1956. Concerning these, Arndt wrote (*5*):

> The most important "refinement" which I used later on is the influence which coplanarity has on mesomerism and resonance energy. This very important knowledge is due exclusively to the quantum mechanical theory of resonance. I had not anticipated it and I do not think it could have been arrived at from chemical evidence alone.

The attached bibliography will serve as a guide to these later papers on mesomerism. It is not intended to be exhaustive, but rather as a guide to the general trend of Arndt's later work on resonance.

It is apparent from the preceding that Fritz Arndt was one of the very first to clearly appreciate the difference between tautomerism and resonance, and to conceive of a stable resonance hybrid structure for aromatic compounds. His contributions to this area of chemical thought have been many and continuous from 1924 until the present.

Acknowledgment

I am indebted to Professor Arndt for many enlightening letters and conversations, and for a large collection of reprints. In particular I wish to acknowledge his several long letters during the summer of 1957, when I requested his assistance in preparing this paper, and the photograph of the early days at Breslau.

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The First Isolations of the Transuranium Elements

A historical survey

Any discussion of the history of the isolation of the transuranium elements would not normally include any mention of their discovery. This is because for the transuranium elements the first evidence for unique chemical behavior—the criterion of discovery—has always been based on experiments in which the quantity of material is so small that it is detectable only because of its radioactive decay. This means that for the transuranium elements the discovery has not coincided with the isolation of the element—as it has for most of the other elements discovered in the past three centuries. When we speak here of the isolation we mean the purification of the element from contaminants and the measurement of a property of the element; tracer methods are excluded and the direct observation of a macroscopic property is implied. Among the transuranium elements this observation has generally been made on a compound of the element rather than the elemental matter itself because of the experimental difficulties inherent in producing reactive metals on a microgram scale.

The six transuranium elements and the years in which they were isolated are neptunium, 1944; plutonium, 1942; americium, 1945; curium, 1947; berkelium and californium, 1958. They will be discussed in the chronological order in which they were isolated.

Plutonium

Plutonium was the first of the transuranium elements isolated. This was done in August and September of 1942 by B. B. Cunningham and L. B. Werner at the Metallurgical Laboratory of the University of Chicago, a unit of the wartime Manhattan District. Cunningham is now Professor of Chemistry at the University of California, Berkeley, and Werner is at the U. S. Naval Radiological Defense Laboratory in San Francisco. The isotope involved in the isolation was the familiar plutonium-239 with a half life for alpha decay of approximately 25,000 years. The isolation followed the discovery of the fissionable isotope by Kennedy, Seaborg, Segre, and Wahl by about 18 months, a period during which all of the investigations of plutonium chemistry had been carried out by tracer techniques.

The three principal objectives of the isolation work were (1) to determine the specific alpha disintegration rate of Pu^{239}, (2) to determine the chemical properties of pure plutonium compounds and the chemical behavior of plutonium solutions at ordinary chemical concentrations, and (3) to demonstrate a chemical process for the separation of plutonium from uranium and fission products. The establishment of a reliable value for the specific activity of Pu^{239} by a direct weighing and alpha-counting method was a prime objective because this figure entered directly into the calculation of the thermal-neutron-fission cross section of the isotope.

A preliminary isolation yielding about one microgram of Pu^{239} was carried out in August, 1942, in order to prove a satisfactory separation and isolation procedure. At the time the isolation was performed it had not yet been shown that a self-sustaining nuclear reaction leading to the production of substantial amounts of Pu^{239} could be carried out, and therefore the plutonium used in the preliminary isolation was produced by the irradiation of natural uranium with neutrons produced by a d,n reaction on beryllium. Five kilograms of uranyl nitrate hexahydrate were irradiated using 12-Mev deuterons from the 60-inch cyclotron at the University of California Radiation Laboratory at Berkeley. The plutonium produced, approximately one microgram, was separated by a series of "fluoride cycles" from uranium and fission products and concentrated with 5 mg of cerium and 5 mg of lanthanum in 15 ml of 0.5 M H_2SO_4. These, and later, bulk separations of the large mass of uranium were carried out at Berkeley by A. C. Wahl and J. W. Gofman and at Chicago by A. H. Jaffey, T. P. Kohman, D. E. Koshland, Jr., and E. H. Turk. The solution of cerium, lanthanum, and plutonium was concentrated by evaporation and the fluorides precipitated by the addition of HF and KF solutions. The fluoride precipitate was then converted to a soluble sulfate by fuming with sulfuric acid and the plutonium oxidized to the "fluoride-soluble" oxidation state by addition of solid argentic oxide. Upon addition of hydrofluoric acid the rare earths were precipitated and the plutonium remained in solution. It was separated and recovered by centrifuging the solution, removing the supernatant, and fuming the supernatant with sulfuric acid to convert the plutonium to a soluble sulfate. Repeated cycles identical to this were carried out with ever smaller quantities of rare earth carrier until finally, on August 18, 1942, a pure sample of plutonium fluoride was precipitated—the first isolation of a synthetic element. This material was not satisfactory for gravimetric work but it did indicate that the fluoride-cycle method was satisfactory for concentrating and purifying plutonium at all concentrations of

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plutonium and rare earth carrier. Accordingly, another isolation was performed on about 30 micrograms of plutonium which had been produced by irradiating 90 kilograms of uranyl nitrate hexahydrate with neutrons produced by the reaction of beryllium and deuterons from the cyclotron at Washington University, St. Louis. In this experiment the bulk of the uranium was removed by ether extraction and the plutonium concentrated by means of successive fluoride cycles with decreasing amounts of lanthanum carrier. Finally the lanthanum was removed by a fluoride precipitation carried out with the plutonium oxidized to the fluoride-soluble state. The plutonium in the supernatant solution was fumed with sulfuric acid to yield soluble plutonium sulfate, the hydroxide was precipitated with ammonium hydroxide and washed and then dissolved with dilute nitric acid. From this solution plutonium iodate was precipitated, metathesized to the hydroxide, dissolved in dilute nitric acid, and reprecipitated. Metathesis of this plutonium iodate to the hydroxide yielded a pure material which was dissolved in dilute nitric acid to give a stock solution of about 20 micrograms of plutonium nitrate with the solution concentration approximately 0.01 *M* in plutonium.

Several small portions of this solution were used for direct-weighing determinations of the specific activity of Pu^{239}. The mass determination was done on a Salvioni type microbalance which had been constructed and calibrated by two independent methods. The first method consisted of constructing two additional Salvioni balances of lesser sensitivity and calibrating the less sensitive of the pair with a standard 1-milligram analytical weight. This calibration was used to determine the mass of a platinum wire, which was then used to calibrate the more sensitive second balance; similarly, a knowledge of the relation between load and displacement for the second balance allowed a calibration to be obtained for the third balance, the most sensitive one and the one on which the plutonium was to be weighed. A check on this calibration was made by an independent method. A 1-liter solution of thorium nitrate was prepared and the concentration of the solution was determined by ordinary analytical techniques. Then a known volume, about 1 microliter, of the solution was delivered onto the previously weighed platinum weighing pan of the Salvioni balance. The pan was then ignited until a constant weight was attained. The two calibrations agreed within 0.3% and indicated a sensitivity of ±0.00126 microgram. On September 10, 1942, the first weighing of a pure compound of a synthetic element was made when an aliquot of the plutonium solution was delivered onto the previously weighed platinum weighing pan, dried, and ignited. The deflection of the balance indicated a weight of PuO_2 of 2.77 micrograms. This material was not used for further experimentation but was preserved intact. Two more weighings were made of PuO_2, sample weights 4.55 and 2.20 micrograms, and these were used for specific-activity determinations which we now know indicated a purity of the plutonium stock solution of >95%. Additional experiments were carried out, using the same plutonium stock solution, to determine the oxidation number of plutonium in plutonium iodate and to determine the approximate solubilities of various plutonium compounds. This information was of importance in connection with the problems involved in designing chemical methods for the large-scale extraction, decontamination, and purification of plutonium. The chemical separations process at Hanford was successful from the beginning of operation and represented a scale-up factor of 10^9 over the ultramicrochemical experiments.

The isolation of plutonium required microchemical techniques of great ingenuity. Both new techniques and the modification of previously developed techniques were used. In the latter the work of P. L. Kirk and associates and M. Cefola and A. A. Benedetti-Pichler should be mentioned.

Neptunium

Neptunium was the first of the transuranium elements discovered, but it was not isolated until about two years after Cunningham and Werner had isolated pure plutonium. The neptunium isolation was carried out at the Metallurgical Laboratory of the University of Chicago by L. B. Magnusson, now of the Argonne National Laboratory Chemistry Division, and T. J. LaChapelle, currently employed in industry in California. Neptunium-237 with an alpha-decay half life of more than one million years was the isotope available. Two objectives stimulated the isolation of neptunium. First, an accurate value for the half life, determined by means of a direct-weighing specific-activity measurement, was desired because of the fundamental importance of this constant and for accurate standardization of the radiometric method of mass determination. In addition, a more accurate and detailed knowledge of the chemistry of neptunium was needed than could be obtained from tracer experiments. It was especially desired to establish one or more of the oxidation states of neptunium along with the formula of a dry compound.

Two sources of Np^{237} yielded approximately equal amounts of neptunium. One source was 64 pounds of uranium metal which had been bombarded by fast neutrons produced by the reaction of beryllium with deuterons from the cyclotron at the University of California Radiation Laboratory, Berkeley. The other source was uranium from a chain-reacting pile. Both sources produced neptunium-237 as a result of the n, $2n$ reaction on uranium-238, which yields the beta-decaying U^{237} of about 7 days half life. A total of 45 micrograms of neptunium was isolated by utilizing the fact that neptunium is precipitated by fluoride ion under certain conditions and yet can be rapidly oxidized to a fluoride-soluble state by bromate ion. The neptunium was separated from uranium by precipitating it, along with lanthanum carrier and plutonium, by adding HF to the solution previously treated with reducing agent. Separation of the neptunium and plutonium was achieved by dissolving the fluoride precipitate and adding potassium bromate. Under the conditions used plutonium was oxidized very slowly, and precipitation of lanthanum and plutonium fluorides left the oxidized fluoride-soluble neptunium in the supernatant. The supernatant solution was then treated with excess sulfur dioxide and the neptunium recovered as a fluoride which could be dissolved by any one of several means. Repeated bromate cycles separated the neptunium from contaminants

until finally a pure neptunium fluoride was obtained. This was dissolved and a hydroxide precipitated. After being washed, the precipitate was fired and ignited and about 10 micrograms of the resulting oxide was scraped into an X-ray capillary. The remaining oxide was recovered and used for further preparation of neptunium compounds and measurement of their solubilities and crystal structure.

An X-ray-diffraction analysis of the ignited neptunium hydroxide was made by W. H. Zachariasen. He obtained a diffraction pattern which showed the oxide to be isomorphous with ThO_2, UO_2, and PuO_2, thus establishing a +4 oxidation state for neptunium. With this information about the preparation of a compound of definite composition, a specific-activity determination was undertaken. Two weighings of 3.82 and 3.75 micrograms of NpO_2 were made on a Kirk, Craig, Gullberg, Boyer quartz-fiber torsion microbalance, with a precision of about 0.02 microgram, and the balance pans then were counted directly in an alpha counter of ~50% geometry. The half life calculated from this specific-activity measurement, 2.20×10^6 years, is within 1% of the value obtained in recent years by using large quantities of Np^{237}, and demonstrates clearly the purity of the neptunium isolated so neatly by Magnusson and LaChapelle.

Americium

Element 95, americium, is the third element following uranium in the periodic table, but it was the fourth transuranium element discovered—following curium, element 96, by a few months—and unlike all the other transuranics it was isolated in the form of pure compounds less than one year after it was discovered. The isolation was carried out at the Metallurgical Laboratory of the University of Chicago by B. B. Cunningham, who three years previously had achieved, in association with L. B. Werner, the isolation of the first synthetic element ever isolated, plutonium.

After the discovery of and prior to the isolation of americium, rather extensive tracer experiments on the chemistry had been carried on by the discoverers, Seaborg, James, and Morgan, and also by Thompson, Morgan, James, and Perlman. These investigations demonstrated the pronounced stability of the tripositive oxidation state of americium and the great similarity between the aqueous tripositive ions of the rare earth elements and americium. In three respects the problem of isolating americium differed from those encountered in the isolations of neptunium and plutonium. First, on the basis of the tracer experiments it appeared that it was difficult, if not impossible, to obtain any oxidation state other than +3 for americium. Also, the only methods of separating americium from the naturally occurring rare earths on a microgram scale involved prohibitive losses. Thirdly, the half life of Am^{241}, the principal isotope, was uncertain by at least an order of magnitude, which meant that the amount of americium expected in the isolation was uncertain, and from an amount obtained there was no way of judging its probable purity. The americium-241 was produced by pile irradiation of plutonium, which by multiple neutron capture produced Pu^{241}, which yielded Am^{241} by beta decay. Necessity for separation of the americium from rare earths was avoided by subjecting the plutonium to extensive purification before irradiation and carefully avoiding any rare earth contamination from reagents or apparatus during the isolation. The americium produced in the irradiated plutonium was concentrated by hydroxide precipitation following precipitation of the bulk of the plutonium as peroxide. This cycle was repeated several times and a final americium-plutonium separation performed by oxidizing the plutonium to the fluoride-soluble +6 state and precipitating the americium fluoride with HF. The americium fluoride was dissolved, and after some further purification a very small portion of the americium solution was subjected to spectrographic analysis carried out by M. Fred and F. Tomkins. Lead and iron were the detected impurities, and these were removed by a lead sulfide precipitation and precipitation of the americium as fluoride to separate it from iron. On the basis of the chemistry which had been carried out on the sample, and from observation of its color, this was believed to be a pure americium compound. This fluoride was therefore used for a direct-weighing specific-activity measurement to determine the half life of Am^{241}. The ignited fluoride yielded a black oxide which was weighed on a quartz-fiber torsion microbalance and then counted in a low-geometry alpha counter. On the assumption that the several micrograms of oxide was AmO_2—an assumption later verified by X-ray-diffraction analysis—a half life of 498 years was calculated. The americium oxide was dissolved off the platinum boat and 20% of it used for spectrographic analysis which indicated 2% La, 0.1% Mg, and 6% Pt, the latter presumably dissolved from the weighing boat when the oxide was dissolved.

The remaining americium was purified and precipitated as hydroxide. The hydroxide was dissolved in dilute nitric acid and used for further studies of the oxidation states of americium in aqueous solution: oxidation states both higher and lower than +3 were looked for without definite success. In addition, the aqueous-solution absorption spectrum of Am(III) was determined. The absorption spectrum tended to verify the validity of Seaborg's actinide hypothesis: the difference between the spectra of americium and plutonium was similar to the difference between the spectra of europium and samarium. This lent weight to the argument of Seaborg that the new elements were part of an actinide series analogous to the rare earth or lanthanide elements.

Curium

The actinide hypothesis also predicted that element 96, curium, would be the seventh member of a series in which the *f* orbitals lay at progressively lower levels. Curium was postulated to be an analogue of gadolinium and a special stability was expected for Cm(III), presumed to have a configuration of seven 5*f* electrons. This had been borne out by tracer studies which indicated that only +3 curium was stable in aqueous solution. The problem of isolating curium from irradiated americium thus resolved itself into one of separating two tripositive ions similar to two adjacent rare earths. This separation and the isolation of curium were successfully accomplished by L. B. Werner, associated earlier with the plutonium isolation, and I. Perl-

man at the University of California Radiation Laboratory, Berkeley.

A quantity of 4.48 milligrams of Am^{241} was irradiated for one year with a high flux of slow neutrons to produce about 150 micrograms of curium-242. The separation of the curium from americium was effected by means of a cation-exchange column using citric acid eluant. Additional ion-exchange separations were made on americium-contaminated fractions until 115 micrograms of Cm^{242} was obtained free of americium in 50 milliliters of solution. This material was concentrated by readsorption on several small portions of ion-exchange resin and then batchwise elution from the resin with citrate solution. After decomposition of the citrate with nitric and sulfuric acids, curium hydroxide was precipitated. Handling Cm^{242}, which decays by alpha-particle emission with a half life of only 162 days, leads to problems other than just those of manipulating small quantities of radioactive material. Decomposition of the aqueous solution occurs as a consequence of the high alpha-decay rate, and both buildup of peroxide and evolution of gas are observed. This gas formation in the solution causes a precipitate to be stirred up within a few seconds after it has been compacted by centrifugation. Another concomitant of the short half life of curium-242 is the growth in the curium at the rate of 0.5% per day of daughter Pu^{238}. Except immediately after a separation plutonium is always present as an impurity.

The curium hydroxide was dissolved and the absorption spectrum of the solution examined. After purification of the curium from plutonium two 1-microgram samples were used for spectrographic analysis, which indicated that only lead was a major impurity. After precipitation of lead sulfide a 5-microgram sample was sparked to obtain a more complete measure of the spectral lines attributable to curium and to check for impurities. A further check on impurities was made by performing a direct-weighing specific-activity determination. Unlike the transuranium elements isolated earlier, the curium-242 had a half life so short that it was known from direct decay observations. A specific-activity determination on curium would thus check the purity of the compound weighed. On the assumption that the composition of the oxide was Cm_2O_3, about 40 micrograms of curium was weighed on a quartz fiber torsion microbalance and then dissolved and counted. A purity of 85 to 93% was found for the oxide preparation.

Berkelium and Californium

In September, 1958, at the 2nd Geneva Conference on the Peaceful Uses of Atomic Energy, a paper was presented entitled "First Macroscopic Observations of the Chemical Properties of Berkelium and Californium." Thus the fifth and sixth transuranium elements have now been isolated. This work was done during the spring and summer of 1958 by B. B. Cunningham and S. G. Thompson at the University of California Radiation Laboratory, Berkeley.

Prolonged neutron irradiation of Pu^{239} produced about a microgram each of berkelium, element 97, and californium, element 98. A mixture of isotopes was produced in each case, but those present in greatest abundance were Bk^{249}, a 300-day β^- emitter, and Cf^{252}, a 2-year α-emitting isotope. Prior to this work by Cunningham and Thompson the only knowledge of the chemical properties of these elements had been obtained by tracer experiments. This knowledge was actually extensive enough to allow the transplutonium elements to be concentrated by means of ion-exchange techniques which had been tested repeatedly. The final purifications of both berkelium and californium also consisted of elution from a very small ion-exchange column. The solution coming off the column passed directly into a capillary cell with optically flat windows, where the absorption spectrum of the elements could be studied. Approximately $^1/_2$ microgram of berkelium and double that amount of californium in dilute HCl were studied in the cell, and revealed no absorption lines in the visible region of the spectrum. The absence of detectable absorption lines of Bk(III) in the visible region of the spectrum was expected, but the absence of lines for Cf(III) suggested that in the heavier (as contrasted with the lighter) actinides the transition probabilities were decreasing for transitions from the $^6H_{15/2}$ ground state to the various ^6F levels. Additional studies of the absorption spectrum of Cf(III) by photographic methods revealed the presence of two broad weak absorptions which may correspond to transitions in analogous states of Dy(III).

Magnetic-susceptibility measurements on tripositive berkelium and californium were also made. The separate ions were sorbed on single beads of Dowex-50 resin and the beads suspended in a magnetic field by means of a plastic basket sealed to a fine quartz fiber. Gd(III) was used as the reference standard. The experimental results agreed best with moments derived on the assumption that the electrons occupy f orbitals and interact by unperturbed pure L-S coupling.

Ten transuranium elements are now known, and of these ten, six have been isolated in amounts such that macroscopic properties could be observed or pure compounds weighed. Element 99, einsteinium, will perhaps be isolated in the near future, but it may well be the last element available in macro quantities. Thereafter the half lives are so short that even if sufficient quantities of the transeinsteinium elements could be produced the isolation would be difficult.

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The Atomic Form Periodic Table

To an outsider, it must appear that the favorite parlor game of many chemists is the devising of new forms of the periodic table of the elements. Being on the inside, we realize that many of the novel forms proposed are based on some different guiding principle that the author feels is important. A certain amount of dissatisfaction with the conventional short and long forms is usually the reason why a chemist enters the game.

This author finds two sources of dissatisfaction. One is the inability of conventional tables to cope geometrically with the increasing length of the periods, which necessitates placing the lanthanide and actinide series in footnotes to the table. This was not as serious in the pre-plutonium era when the rare earth elements were *rare* and the actinides not recognized as a similar series. With pure lanthanides becoming increasingly available, and the new actinides assuming *world-shaking* proportions, footnotes hardly seem to be appropriate positions for these two important series.

The other inadequacy of conventional tables is their failure to make sufficiently clear to students the relationship between atomic structure and physical and chemical properties. While the connection is there, it is not readily apparent. The reason for this is quite obvious historically, since the conventional tables originated with Mendeleev in 54 B.Q.M. (*Before Quantum Mechanics*). While he put the chemists far ahead of the physicists in understanding the atom, it must be conceded that the physicists have caught up. As yet, the two periodic tables in commonest use do not reflect this concession.

Some Solutions to the Problem

Two geometrical arrangements that provide more space for elements as the periods become longer, obviating the necessity for footnotes, are the spiral and circular forms. The spiral form, both two-dimensional and three-dimensional, has been proposed many times. One disadvantage is that the periods run into one another without separation. Another is that this form does not connect atomic structure and periodicity.

Numerous circular tables are listed in Mazurs' book.[1] Since the one about to be described is essentially the long table bent into a circle, no great originality is claimed for its geometry, though its group numbering is thought to be unique and more useful. However, the choice of arrangement is more than a matter of geometrical convenience; correlation between a table in concentric circles and the structure of the atom is possible. Therefore the author likes to call it an *atomic form table*. Cabral[2] recognized this point in calling his table the *Natural Classifications of the Elements*.

The Atomic Form

Before assembling an atomic form table, it is well to recognize that there is a choice of a guiding principle to make. It is necessary to decide which is more fundamental atomic structure or chemical properties. Resolving to be completely objective, we must champion the side of physics and admit that the relation is best conceived as one of cause and effect, with atomic structure determining chemical properties. Consequently, it is desirable to construct first a table that is periodic with respect to atomic structure. Chemical periodicity will then be assured and a notation useful to chemists can be superimposed.

Figure 1 shows how the atomic form is begun, the element symbol being placed in the position of the added electron. This process is continued (Fig. 2) up to calcium, which can be deduced to have the structure 2-8-8-2 by counting the symbols preceding it. The symbol of scandium (2-8-9-2) cannot be put in the shell of the added electron without making it appear to follow magnesium. Therefore it is written in the same arc as calcium and the region enclosed within an outer boundary marked II-A[3] to indicate that, like calcium, it has two electrons in its outer shell. Of course, this actually results in a conventional long-form table bent into a circle but with the lanthanides and actinides inserted in their rightful places. However, the group numbering (Roman numerals) is different, being (with a few minor exceptions) the number of electrons in the outer shell. For chemical purposes (next section) it is best to consider that the inert elements have no electrons in their outer shell (Group 0).

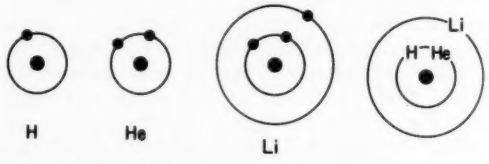

Figure 1. Starting the table.

Chemical Considerations

So far, this provides a purely physical table, but the chemical significance of Group II-A is striking. With a

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[1] MAZURS, E. G., "Types of Graphic Representation of the Periodic System of the Elements," E. Mazurs, La Grange, Ill., 1957.

[2] Bol. didático escola agron. Elisen Maciel, Inst. agron. Sal (Pe lotas, Brazil) No. 1, 3–6 (1951).

[3] *A* is used because there is also a Group II-B.

few exceptions, all elements in this group exhibit an oxidation state of +2. This fact is not brought out by group numbers in conventional tables.

Pursuing this point further, it is also a fact that +2 is the *lowest* oxidation state (other than zero) of the elements in this group. Similarly, +1 is the lowest oxidation state of the elements in II-B, while the other group numbers are the *highest* oxidation states for their elements (+4 for Pb, +5 for Bi, etc.). This suggests adding a second (arabic) group number to give the *range* of oxidation states. In the lefthand side of Group II-A, this will be the conventional group number. Lower limits to the oxidation states of the metals in Groups III to VI are placed along the dotted metal–non-metal boundary. Recurring subgroup numbers in Group II-A are differentiated by letters: 3A, 3B, 3C, 4A, 4B, etc.

On looking at the table, a student can deduce that the oxidation states of manganese (Group II-A:7) range from +2 to +7, osmium (Group II-A:8) from +2 to +8, hydrogen (Group I-C:−1) from +1 to −1, etc. Exceptions can be found but are not numerous, for instance, +6 is the upper oxidation limit for iron (not +8) and +3 for gold, (not +2). Another type of exception, caused by forcing the elements into an oversimplified pattern, is that the ground states of Cr, Nb, and Mo have only one electron in their outer orbits. However, the chemical fact that is of more significance is that they lose two electrons but not just one (in stable compounds).

Hydrogen, always a misfit, is placed in line with the halogens because it has a range of oxidation states that is analogous to the halogen range of +7 to −1 (Group VII:−1), but limited by its atomic structure, to a maximum of +1. On the basis of range of oxidation states, placing hydrogen in group I-A:1 with the alkali metals would be illogical. Similarly, the inert element group is best designated as 0:0, rather than VIII:0.

The lanthanide and actinide group numbering requires further comment. While exceptions to the indicated ranges of oxidation states occur, the enlarged subgroups, e.g., II-A:6A, bring together similar elements: U (+2, +3, +4, +5, +6), Np (+3, +4, +5, +6), Pu (+3, +4, +5, +6).

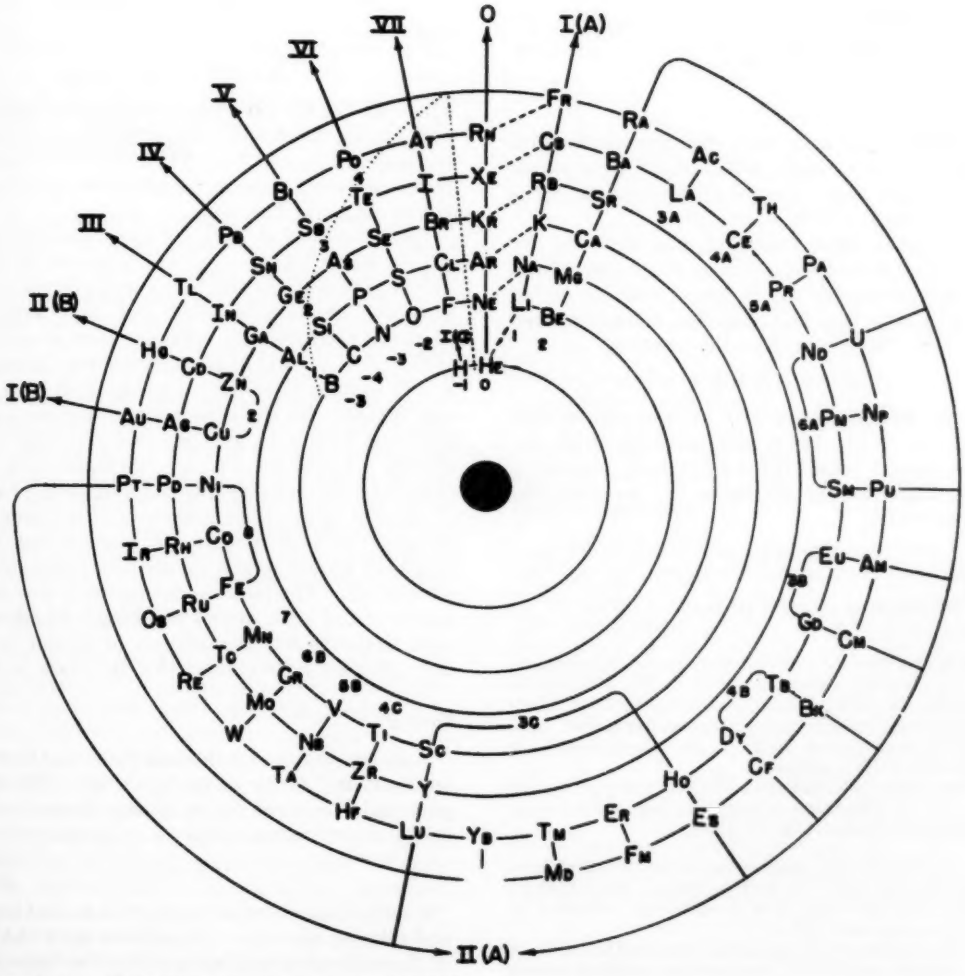

Figure 2. Periodic table, "atomic form." Copyright 1958.

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Ion-Molecule Reactions

The study of the reactions between gaseous ions and molecules is currently the subject of renewed activity, both because of its intrinsic interest and because of its fundamental significance to radiation chemistry. Important contributions toward understanding the physical interactions between ions and molecules appeared more than 50 years ago. The possibility of chemical reactions being controlled by these forces was proposed and developed by Lind and his collaborators in terms of a cluster between an ion and one or more molecules (*1*). The following simple example illustrates the type of mechanism proposed to account for the observation by Lind and Bardwell (*2*) that methane yields hydrogen and ethane under the influence of ionizing radiations.

$$CH_4^+ + CH_4 \rightarrow (CH_4)_2^+$$
$$(CH_4)_2^+ + e^- \rightarrow H_2 + C_2H_6$$

Early Work

Recent observations from mass spectrometry confirm the formation of a complex ion $(CH_4)_2^+$ as a short-lived intermediate and indicate alternative reactions leading to the formation of ethane.

The first ion-molecule reaction was reported by Dempster (*3*) in 1916, upon the basis of his observation that hydrogen produced ions at mass-to-charge ratios[1] of 1,2, and 3, viz., H^+, H_2^+ and H_3^+. He suggested that the ion H_3^+ was formed by the reaction[2]

$$H^+ + H_2 \rightarrow H_3^+$$

This proposal was consistent with his observation that the abundance of H_3^+ decreased markedly with decreasing pressure as required for a two-body process.

In 1928 Hogness and Harkness (*4*) reported the analogous reactions

$$I_2^+ + I_2 \rightarrow I_3^+ + I$$
$$I_2^- + I_2 \rightarrow I_3^- + I$$

as well as the electron transfer processes

$$I^+ + I_2 \rightarrow I_2^+ + I$$
$$I^- + I_2 \rightarrow I_2^- + I$$

The observation (*5*) in 1928 of the hydronium ion by mass spectrometry is of particular interest. This

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

mode of formation of H_3O^+ permits us to conclude that it is very stable with respect to dissociation to H^+ and H_2O, as discussed later.

Another type of ion-molecule interaction commonly encountered in early work was the induced dissociation resulting from collision between the fast ion and a molecule (*6*), as

$$H_2^+ + H_2 \rightarrow H^+ + H + H_2$$

and even

$$H_3^+ + H_2 \rightarrow H^+ + 2H_2$$

The evidence for these processes was the appearance of peaks in the mass spectrum at positions corresponding to masses of $^1/_2$ and $^1/_3$. These could be accounted for by decomposition occurring after ion acceleration but before magnetic dispersion.

Under somewhat different experimental conditions, gas discharge ion sources, which favored multiple collisions between ions and molecules, yielded evidence of extensive reaction between ions and molecules (*7*). Methane produced not only the usual one-carbon ions (CH_n^+, $n = 4$ to 0) but also a two-carbon group ($C_2H_n^+$, $n = 4$ to 0), a three-carbon group ($C_3H_n^+$, $n = 3$ to 0) and others. By the same method, mixtures of $CH_4 + H_2O$ and $CH_4 + O_2$ gave rise to C_2O^+, CO_2^+ and other species. A mixture of $CO_2 + H_2$ resulted in CH_3^+ and other ions, presumably due to ion-molecule reactions.

Another relevant phenomenon of a rather different character is ionic mobility of gaseous ions which has long been known to give evidence of ion-molecule interactions (*8*). The facts do not permit a precise identification of the ionic species resulting. It appears, however, that ions A in the presence of dipolar molecules B may produce ionic clusters $A^+ \cdot B_n$ where $n = 1$ to 6.

Theory

The mobility of ions through gases was described theoretically in 1905 by Langevin (*9, 10*). The long-range potential V between an ion of unit charge e and a molecule of electric polarizability α at distance r is

$$V = e^2 \alpha / 2r^4 \qquad (1)$$

For an ion of mass m to "capture" a molecule of mass M and relative velocity v into a stable orbit the trajectory of the molecule must be such that the linear projection lies at a critical distance b_0 (see Fig. 1) from a parallel

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Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11–1)-38.

[1] In this experiment, as in most others to be described here, gaseous ions were produced by electron impact, accelerated by electric fields and dispersed into a spectrum according to mass/charge by a magnetic field.

[2] The ion H_3^+ is now attributed to the reaction $H_2^+ + H_2 = H_3^+ + H$ because exothermic combination reactions usually require a third body to remove the excess energy.

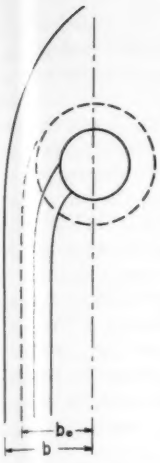

Figure 1. Ion-molecule trajectories as a function of the parameter b. Collision occurs for $b < b_0$.

line drawn through the center of the ion. Then it can be shown, from the necessary balance of centrifugal and attractive forces, that

$$b_0 = (4e^2\,\alpha/\mu v^2)^{1/4} \qquad (2)$$

where

$$\mu = \frac{mM}{M+m}$$

Orbits for which $b > b_0$ (Fig. 1) result in more or less scattering but do not lead to collision. For all orbits with $b < b_0$, collision ensues. The effective cross-section σ for collision is therefore πb_0^2 and it follows immediately from equation (2) that

$$\sigma = \pi b_0^2 = (2\pi\, e/v)(\alpha/\mu)^{1/2} \qquad (3)$$

It should be observed that σ decreases rapidly with increasing velocity, as would be the case for an ion formed in the electric field of a mass spectrometer. As an indication of the magnitude of σ, this quantity may be evaluated for the case $H_2^+ + H_2$ using $\alpha_{H_2} = 0.8 \times 10^{-24}$ cc, $\mu = 1.7 \times 10^{-24}$ g, and $v = 10^5$ cm sec^{-1} to give $\sigma = 210 \times 10^{-16}$ cm^2. The rate of this reaction, which can be followed through ortho-para hydrogen interconversion, was calculated more elegantly by Eyring, Hirschfelder, and Taylor (*11*). For collision between neutral molecules of hydrogen the collision cross section is 5×10^{-16} cm^2. This greatly enhanced cross section in the former case is the result of the long-range attractive forces between ions and molecules while the gas kinetic cross section results from short-range repulsive forces.

The Mass Spectrometer

Since most of our information concerning ion-molecule reactions comes from mass spectrometry, a brief description of the experimental aspects is essential. In one common type of mass spectrometer (Fig. 2) electrons are emitted from the heated tungsten filament F, accelerated by a potential difference V_i (the ionizing voltage), collimated by appropriate slits and a magnetic field H, and collected by an electrode a. When gas at low pressure (*ca.* 10^{-6} mm) is present in the box traversed by the electron beam (the ionization chamber), some ions of mass m and charge e are formed by electron impact when V_i is sufficiently large. These ions are ejected through the slit s by a small potential difference V_r between the repeller electrode r and electrode b. They are then subjected to the accelerating voltage V_a applied between electrodes b and c, deflected through 180° and radius R by the magnetic field H, and focused upon an ion collector electrode (not shown). The spectrum of mass peaks is usually scanned by sweeping V_a at fixed H according to the relation (for singly charged ions)

$$m = 4.82 \times 10^{-5} R^2 H^2 V_a^{-1}$$

employing atomic mass units, cm, oersteds and practical volts.

At 10^{-6} mm in the ionization chamber, the molecular mean free path is $\sim 10^4$ cm and collisions between ions and molecules are rare. The ions observed arise only from the direct consequences of electron impact, viz., as a result of unimolecular decomposition. No ion current flows unless the energy of the electrons exceeds a critical value. The minimum ionizing voltage V_i required to remove an electron from a molecule is its *ionization potential IP*. For hydrogen it is 15.44 v (*12*).

$$H_2 + e^-(15.44\text{ v}) \rightarrow H_2^+ + 2e^-$$

The minimum ionizing voltage required to produce a particular fragment ion is its *appearance potential AP*. For H^+ it is 18.05 v.

$$H_2 + e^-(18.05\text{ v}) \rightarrow H^+ + H + 2e^-$$

The appearance potential of H^+, or of any other fragment ion, depends upon its origin since by Hess' law it

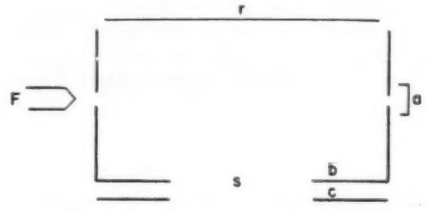

Figure 2. The ionization chamber of a mass spectrometer.

may be regarded as the sum of the processes of dissociation and the ionization, thus

$$RH \rightarrow R + H$$
$$H + e^- \rightarrow H^+ + 2e^-$$

Thermochemistry

Mass spectrometric energy measurements (viz., *IP* and *AP*) have relative, but not absolute, reliability due to uncertainty in the absolute measurements of V_r. The energy scale must be calibrated using atoms or molecules of known ionization potential, and the validity of such measurements has been verified for many cases by comparison with spectroscopic values. The heat of formation ΔH_f of a molecular ion, by usual thermochemical conventions, is taken as ΔH_f (molecule) + *IP*. Thus for the reaction

$$CH_4 + e^- \rightarrow CH_4^+ + 2e^-$$

the relation is $\Delta H_f(CH_4^+) - \Delta H_f(CH_4) = 13.12$ ev.[3] The reliability of mass spectrometric appearance potentials must be tested indirectly, usually by consistency

[3] One electron volt per molecule corresponds to 23,071 cal/mole. Values of ΔH_f for ions, as well as values for *IP* and *AP* used here, are from collected data in ref. (*12*).

in ΔH_f (ion) from different reactions. For one reaction producing CH_3^+,

$$CH_4 + e^-(14.39\text{ v}) \rightarrow CH_3^+ + H + 2e^-$$

we obtain, by identifying $\Delta H_{reaction}$ with $AP = 14.39$ v,

$$\Delta H_f(CH_3)^+ = \Delta H_{reaction} - \Delta H_f(H) + \Delta H_f(CH_4) = 262 \text{ kcal/mole}$$

Another process is

$$CH_3Br + e^-(12.83\text{ v}) \rightarrow CH_3^+ + Br + 2e^-$$

leading to a confirmatory value according to

$$\Delta H_f(CH_3^+) = \Delta H_{reaction} - \Delta H_f(Br) + \Delta H_f(CH_3Br) = 261 \text{ kcal/mole}$$

The following thermochemical cycle is based upon the principle that ion-molecule reactions, to be observed in a mass spectrometer, must have zero activation energy. The formation of H_3O^+ below is therefore not endothermic and we can arrive at a minimum value of the energy of dissociation of the hydronium ion.

$H_2O + e^- \rightarrow H_2O^+ + e^-$	12.61 ev
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	$\gtrsim$ 0
$H^+ + e^- \rightarrow H$	− 13.60 ev
$H + OH \rightarrow H_2O$	− 5.16 ev
$H^+ + H_2O \rightarrow H_3O^+$	$\gtrsim$ − 6.15 ev

Criteria

As an approximation adequate for our purpose, the measured ion current i ("peak height") at normal pressure is proportional to the number of ions n of the corresponding mass produced per unit time. Also, the ion current at a given m/e is proportional to the partial pressure of the molecular species producing the ion. Thus in a mixture of CH_4 and C_2H_6, at partial pressures P_{CH_4} and $P_{C_2H_6}$ we have

$$\frac{i_{CH_4^+}}{i_{C_2H_6^+}} = \frac{n_{CH_4^+}}{n_{C_2H_6^+}} = \frac{P_{CH_4}}{P_{C_2H_6}} \qquad (4)$$

When a gas, or mixture of gases, is present in the ionization chamber of a mass spectrometer at relatively high pressure, all peaks previously observed at low pressure are proportionately increased, and relatively small peaks appear which were not formerly observed. This behavior is, of course, characteristic of minor impurities and, if so, we expect to find the new peak heights proportional to the total pressure. It is significant that some peaks increase with the square of the pressure which is characteristic of second order rate processes, and this strongly indicates ion molecule reactions. Examples of mass peaks which show this dependence are m/e at 3 from H_2, at 19 from H_2O, at 17 and 29 from CH_4, and 22 and 34 from CD_4.

Let us consider further the ion at $m/e = 22$ from CD_4 which we identify tentatively as CD_5^+. There are several possible reactions including

$$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3 \qquad (5)$$

$$CD_3^+ + CD_4 \rightarrow CD_5^+ + CD_2 \qquad (6)$$

If reaction (5) is involved in the formation of the secondary ion CD_5^+, then its appearance potential should be 13.26 v, the same as its parent ion, CD_4^+. Similarly, if reaction (6) is responsible for CD_5^+, then its appearance potential will be 14.39 v, the same as CD_3^+. If the correct primary ion is CD_2^+, CD^+ or etc., the expected appearance potential of CD_5^+ would correspond. The observed value is 13.2 v and reaction (5) is indicated. In general, the parent ion-daughter ion relationship can be established upon the basis of their appearance potentials.

To obtain an equation which accounts for the experimental facts it should be recalled that ions originate in the electron beam (Fig. 2). Under the influence of the weak repeller field ions accelerate slowly toward electrode b in a nearly straight line of length l. Their relatively low velocity within the ionization chamber favors collision with molecules. Once ions reach the slit s (Fig. 2) they acquire a high velocity and collision is improbable (eq. 3). The familiar development of the simple equation for the frequency of gaseous collisions (*13*) serves as a pattern for collisions between ions and molecules. It is qualitatively clear that the number of secondary ions produced per unit time n_s^+ is proportional to the number of primary ions n_p^+, to the effective path length of the primary ion l, to the phenomenological reaction cross section Q and to the number of molecules per unit volume, N. That is

$$\frac{n_s^+}{n_p^+} = QNl \qquad (7)$$

Measured reaction cross sections at ion energies of about 1 ev., as calculated by equation (7), are commonly in the range 50–200 $\times$ 10^{-16} cm^2 and are independent of temperature. Both of these facts are consistent with equation (3).

Recent Work

The dependence of reaction cross section upon ion velocity, in terms of the repeller field strength, is illustrated for several reactions in Table 1 from recent work of Field, Franklin, and Lampe (*14*) and of Stevenson and Schissler (*15*). These results demonstrate qualitatively the decreasing cross section with increasing ion velocity. The first three reactions in this table, and others involving hydrocarbons, do not obey equation (3) as regards the dependence upon velocity (or, what amounts to the same thing, $V_r^{1/2}$). The fourth reaction listed is representative of many reactions reported (*15*).

Table 1. Cross Sections in Cm^2 $\times$ 10^{16} at Various Repeller Field Strengths

	60	20	8	v/cm
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$[a]	15	45	66	
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$[a]	17	46	59	
$C_2^+ + C_2H_4 \rightarrow C_4H_3^+ + H_2$[a]	28	58	97	
$Ar^+ + H_2 \rightarrow ArH^+ + H$[b]	47	76	113	

[a]From ref. (*14*); [b]by interpolation, from ref. (*15*)

At this time there has been little application of known ion-molecule reactions to account for the facts of radiation chemistry. There is good evidence (*16*) that the efficient radiation polymerization of acetylene (*1*) is at least partly due to a succession of reactions of the type

$$C_xH_y^+ + C_2H_2 \rightarrow C_{x+2}H_{y+2}^+$$

A limited study of the radiation of chemistry of methane strongly suggests that the efficient formation of ethylene, ethane, and higher hydrocarbons is governed by the reaction (*17*)

$$CH_5^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

Mass spectrometry is a powerful tool for the development of radiation chemistry, but it has important limitations. One is that an ion can only be observed some 10^{-6} sec after its formation and many unstable species have already disappeared. The second is that binary encounters are fairly difficult to observe, ternary or successive binary encounters are practically impossible to detect. In gases at normal pressures an ion undergoes collision within *ca.* 10^{-10} sec of formation, which may remove energy and stabilize species that do not survive at low pressure in the mass spectrometer. Also, reactions which are too inefficient to be observed in the mass spectrometer may still be quite fast, by conventional criteria, at ordinary pressures.

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Physical observation of Radiation-Induced Intermediates

In studying the radiation chemistry of a system the obvious initial step is to determine qualitatively the various new substances formed during irradiation. This is logically followed by more detailed quantitative analyses establishing radiation chemical yields for the various products. This information is hardly sufficient for a complete understanding of the system. A more fundamental understanding comes only with a detailed consideration of the mechanisms of the various reactions that take place.

Reaction intermediates and mechanisms are often speculated upon when only the products are known. Yield values give a more stringent set of conditions that may allow some choice among proposed models. The problems of furthering the understanding now become much more formidable for it must be remembered that, in general, the intermediates have only fleeting existence and cannot be isolated by the usual chemical methods. Considerable progress using chemical methods, nonetheless, can be and has been made. Mechanism models are often tested by varying the conditions under which the radiation experiment is carried out and by altering the chemical nature of the system. The effect on the nature or abundances of the various products is then a test of the various proposed intermediates and mechanisms. Often considerable evidence can be gathered that supports a specific model involving participation of certain intermediates and a specific mechanism. Unfortunately, such models often lack uniqueness.

The desirability of characterizing and studying the intermediates by physical means is obvious. There are several needs. First, one would like physical evidence for the existence of a species which may be proposed as an intermediate in a chemical system. The properties of the species as elucidated by physical measurements would then be of interest. Much of this type of information has come from studies in which the intermediate has not been formed by irradiation. Moreover, it has frequently been necessary to borrow this information from studies on systems that are quite different than the one of immediate chemical interest. For example, the free radical HO_2 has been proposed as an intermediate in the chemistry of certain irradiated aqueous systems, but the direct physical evidence for its existence and knowledge of some of its properties come from gas phase, mass spectrometry studies (*1*). Thus our ideal would be to have physical measurements that have been made concurrently with the radiation

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[1] Operated for the United States Atomic Energy Commission by the Union Carbide Corporation.

chemistry study. These measurements would not only identify and characterize but would also assay the intermediate. This ideal has not, in general, been reached, but it appears that definite steps in that direction have been taken.

The various spectroscopic techniques have been most useful in observing the types of intermediates formed by radiation processes. The intermediates most frequently examined have been free radicals and atoms. Mass spectrometry studies on gas phases have been made where some of the methods of forming the intermediate have been pyrolytic, by electric discharges, photochemical or by flames. Similarly, the optical absorption spectra (particularly in the visible and ultraviolet) have been studied for a number of both simple and complex species in the gas, liquid, and solid phase. The use of flash photolysis has been a particularly important method of formation in optical studies.

Work on the solid phase has been particularly attractive because of the ease with which reactive species may be stably trapped at a low temperature. High concentrations of labile species have been formed in solids at low temperatures by irradiation, photolysis (both by flash and continous illumination), and by condensing products of pyrolysis or products formed by an electric discharge. The usual methods of observation have been with optical absorption spectroscopy or with paramagnetic resonance. The feasibility of trapping labile species in solids has recently given a great impetus to the physical study of radiation-produced intermediates. Some aspects of the paramagnetic resonance method and the results of a few experiments will be described here. Although the use of the method for radiation-produced intermediates thus far has been for stably trapped concentrations, there is promise that the method can be used on liquid systems during the course of extremely intense irradiation.

The Paramagnetic Resonance Method

The paramagnetic resonance method is generally applicable as a means of detecting any type of unpaired electron system whether it be in the solid, liquid, or gas phase. Chemical free radicals, certain free atoms, and perhaps such solid-state entities as F centers are those of greatest interest in radiation chemistry. The method is based upon the magnetic properties that these entities have by virtue of their containing an unpaired electron. (Such species may contain more than one unpaired electron, but for simplicity only one will be considered here.) The paramagnetic resonance experiment is carried out by placing the sample of interest in a uniform magnetic field. The field interacts with the magnetic moment of the unpaired electron and causes the electron spin to orient in the magnetic field. The spin of a single unpaired electron may orient in either of two directions (quite unlike the classical compass needle which always points north in the earth's field and not either north or south). These two orientations correspond to different energy states of the electron, and all of the unpaired electrons will have their spins divided between the two orientations (energy states). The division is not equal, however, there being a greater number of spins in the lower energy state. The division depends upon the temperature of the sample and the difference of energy between the two states and is given by the Boltzmann distribution. The energy difference between the two states is given by $\Delta E = g\beta H$, where H is the strength of the magnetic field (gauss), β is the Bohr magneton (a fundamental unit of magnetic moment, $\beta = 0.927 \times 10^{-20}$ erg/gauss), and g is the spectroscopic splitting factor which is a dimensionless number the value of which depends upon properties of the unpaired electron. The g value for a free electron is 2.0023. The paramagnetic resonance experiment is completed by allowing the sample to experience radio frequency energy of a frequency ν such that $\Delta E = h\nu$, where h is Planck's constant (6.625×10^{-27} erg–sec). Satisfying this condition causes electron spins to make transitions from the lower to the higher energy state (the spin flips its orientation). With the proper electronic instrumentation this absorption of radio frequency energy can be detected as a spectroscopic absorption line. The basic equation for the phenomenon is, then, $h\nu = g\beta H$. With this equation it may easily be seen that for g values in the vicinity of 2 and with convenient laboratory fields (thousands of gauss) ν will be a microwave frequency. An electron with a g value of 2 in a field of 3200 gauss requires a frequency of 9000 Mc to achieve resonance (to see an absorption). Since it is more convenient to vary the strength of a magnetic field than a microwave frequency, spectrometers are built to operate at a fixed frequency and the magnetic field is varied until an absorption line is observed. A measurement of the strength of the field and the frequency will then allow the g value to be calculated. The instrumentation is often arranged to display the spectra either on an oscilloscope as intensity of absorption versus field strength or on a chart in which case the operating principle usually requires recording of the derivative of intensity of absorption versus field strength.

If one randomly selects a large number of substances, cools them to, say, liquid nitrogen temperature, irradiates with, say, gamma rays and examines in a paramagnetic resonance spectrometer a large number will show interesting spectra. Some solid substances, especially the more complex ones, do not require cooling in order to observe a spectrum. Frequently samples show several absorption lines. These may arise either from more than one kind of unpaired electron species or, partly for reasons to be indicated later, from a single species. The spectra usually appear with g values in the vicinity of 2. This is characteristic of many chemical free radicals but is by no means an exclusive property of free radicals. The amount of a species present (number of unpaired electrons in the sample) can be deduced from the area of the absorption line, but high accuracy is achieved only with great difficulty. If the samples are warmed the spectra vanish. In some cases this is because the species react to form the final products that the radiation chemist finds in his assays. Often the rate at which spectra vanish after warming may be determined and something said about the order of the reaction and about the activation energy. In some cases features of the spectrum will allow something to be said about the identity of the species. In favorable cases a rather complete identification can be made. There are many ramifications to such studies, and it is only possible here to refer briefly to some of

those that have a bearing on radiation chemistry. These points will be illustrated more fully by examples given below.

Atomic Hydrogen

A sample of sulfuric, phosphoric, or perchloric acid cooled to liquid nitrogen temperature (77°K), irradiated with gamma rays from a Co^{60} source and then examined while still cold will show several paramagnetic resonance absorption lines. The spectra center at $g = 2$. The spectra for each of the acids are different except for one characteristic pair of lines that are spaced by about 505 gauss. These lines have been shown to originate from atomic hydrogen (*2*) stably trapped within the solid acid. There are two lines rather than one as a result of a hyperfine interaction between the unpaired electron of the atom and the nucleus. The proton with nuclear spin $I = {}^1/_2$ has a magnetic moment, and its spin is oriented in the applied magnetic field in a manner similar to that for the electron. A nucleus will orient in $(2I + 1)$ ways so the proton will have just two states. The magnetic field experienced by the electron will be the externally applied field with a contribution from the magnetic moment of the proton. This contribution will either add to or subtract from the externally applied field depending upon which of the two states the proton happens to be in. Since the protons are divided almost equally into the two states the absorption line will be split into two parts of essentially equal strength. In order to see if the pair of lines was, indeed, due to a hyperfine interaction the original experiments were repeated with deuterium replacing part of the normal hydrogen. The deuteron has a spin $I = 1$ and thus it has three states in a magnetic field. Three lines would be expected, and these were seen. The three lines for atomic deuterium were not spaced as far apart as were the pair for atomic hydrogen. This was expected because the deuteron has a much smaller magnetic moment, and, hence, the additional fields experienced by the electron were much smaller. Polyatomic species containing hydrogen could give the observed results described thus far. These observations have shown that an unpaired electron species is present and that it contains a single interacting hydrogen nucleus. Multiple hydrogen nuclei that interact simultaneously with a single electron give more complex spectra as indicated later. The data completing the identification of the species as atomic hydrogen come from a quantitative measure of the spacing of the lines. This spacing (strength of hyperfine interaction) is a measure of how intimately the electron is associated with the proton. The value for atomic hydrogen is well established from atomic beam measurements (*3*) and represents somewhat of a limiting case for the maximum value an electron interacting with a proton can have. In other words, about the tightest way to couple an electron with a proton is to have the hydrogen atom rather than, say, any free radical. The hyperfine interaction in the irradiated acids is within one per cent of the atomic beam value for atomic hydrogen. Figure 1 is an oscilloscope photograph showing the three atomic deuterium lines in sulfuric acid irradiated at 77°K with gamma rays. The central line appears at the free electron g value. The broad line results from species that have not been identified.

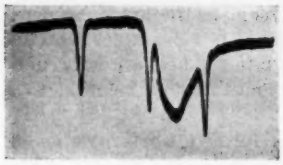

Figure 1. The three atomic deuterium lines for sulfuric acid diluted with heavy water and irradiated at 77°K with gamma rays.

Once the species were identified as being atomic hydrogen numerous experiments were carried out. Upon warming these irradiated acids the atomic hydrogen vanishes at a very low temperature. In sulfuric acid, for example, the atoms react and disappear within a few minutes at −170°C. The spectra for other paramagnetic species that form in these acids do not disappear until a much higher temperature is reached. The rate of disappearance of atomic hydrogen in the three acids has been measured (*4*) at various temperatures. The rates are second order with respect to atomic hydrogen concentration with activation energies of several kcal/mole.

Molecular hydrogen is one of the usual products formed upon irradiating aqueous systems. The second order kinetics for the disappearance of atomic hydrogen upon warming these irradiated acids suggested that the atoms were combining to give hydrogen molecules. In order to test this notion samples of various concentrations of the acids were irradiated at 77°K. Some samples were assayed for atomic hydrogen while others were warmed, melted, and the gases collected and assayed for molecular hydrogen (*5*). Only relative atomic hydrogen assays have thus far been completed, but there is a strong dependence of the yield upon acid concentration. A strikingly similar dependence is seen for the molecular hydrogen yield from similarly irradiated acids. Results for perchloric acid are shown in Figure 2. The principal region of lack of correlation is near

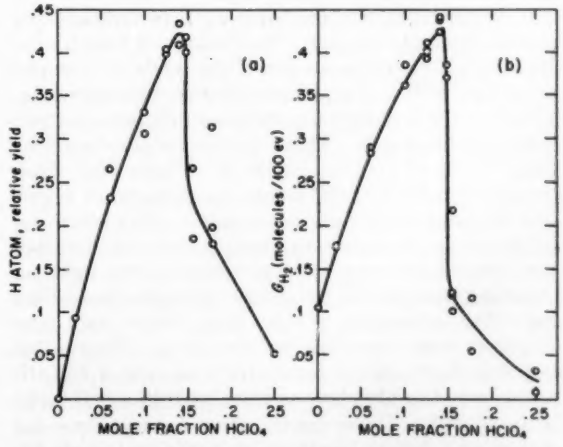

Figure 2. Atomic and molecular hydrogen yields for perchloric acid solutions irradiated at 77°K with Co^{60} gamma rays. (a) Relative atomic hydrogen yields at 77°K. (b) Molecular hydrogen yields after melting.

and at zero acid concentration (ice) where a small molecular hydrogen yield is obtained, but where no stably trapped yield of atomic hydrogen is found at 77°K (*4*). Recently evidence has been found (*6*) for atomic hydrogen in ice irradiated at 4°K. This lower temperature is needed to stably trap the atoms in ice, and possibly quantitative assays would bring the data of Fig-

ure 2 into even closer agreement in the low concentration region. This is one of the few examples where a radiation produced intermediate has been directly identified by physical measurements and its relation to a final product demonstrated.

Atomic hydrogen is also formed upon irradiating Pyrex glass as well as other glasses at 77°K (*4*). The source of the hydrogen is adsorbed water. It is presumably strongly bound, chemisorbed water since it can only be exchanged with heavy water at a slow rate and is not completely removed after several hours at 350°C in a high vacuum. Some commercial brands of fused silica will show the same behavior. In addition, atomic hydrogen has now been seen in a number of other chemical substances irradiated at a low temperature. Other paramagnetic species are usually seen as well.

Methanol and Ethanol

Another example illustrative of the paramagnetic resonance method is a study of the intermediates formed in methanol and ethanol by gamma ray irradiation (*7*). These substances, including some of the deuterium substituted alcohols, have been cooled to glasses at 77°K, irradiated with gamma rays from Co^{60} and examined while still cold. Multiple line spectra are seen, and these are caused, in part, by hyperfine interactions of the unpaired electron with hydrogen. In general, if an electron interacts with n hydrogen nuclei (or any other nuclei with $I = {}^1/_2$) in an equivalent manner (and isotropically) there will be $n + 1$ hyperfine lines. The relative intensities will be as the coefficients of the binomial expansion. Thus two interacting protons will give a spectrum with relative intensities 1-2-1, a 1-3-3-1 spectrum results from three protons, and a 1-4-6-4-1 spectrum results from four. More than one kind of paramagnetic species can be formed in the alcohols which causes still a greater number of lines to be seen.

If the alcohols are irradiated at 77°K in darkness they become intensely colored. This color will bleach after illumination with incandescent light while the samples are still at 77°K. A paramagnetic resonance associated with the color is observed as well as a spectrum that persists after bleaching. These spectra are illustrated for CH_3OH and CH_3OD in Figure 3. Figure 3(*a*) shows the spectrum for CH_3OD before bleaching while Figure 3(*b*) is the same sample immediately after bleaching. In obtaining these data the sample was not disturbed nor the spectrometer settings altered; the light for bleaching was piped to the sample through a fused silica rod. The intensities of the lines before and after bleaching may, therefore, be compared. Figures 3(*c*) and 3(*d*) show similar results for a sample of CH_3OH before and after bleaching and the intensities may again be compared. These spectra show a basic three-line pattern and, before bleaching, an additional single line almost centered on the basic three-line pattern. This superimposed line associated with the colored alcohol is much sharper in CH_3OD (Fig. 3(*a*)) than in CH_3OH (Fig. 3(*c*)). The three-line spectrum, as judged from those lines that are resolved, becomes much stronger upon bleaching. Therefore, it appears that the line associated with the color is, in some sense, a precursor for at least a portion of the paramagnetic species that gives the three lines.

Similar observations have been made on ethanol.

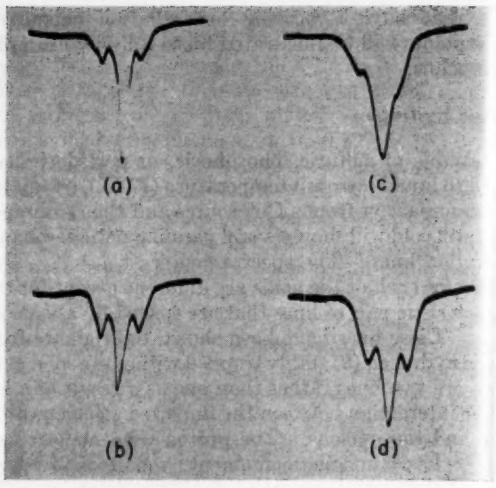

Figure 3. The spectra from methanol irradiated as a glass in darkness at 77°K with gamma rays and examined at ≈64°K. (a) CH_3OD before bleaching. (b) CH_3OD after bleaching. (c) CH_3OH before bleaching. (d) CH_3OH after bleaching.

Colored ethanol contains an extra line almost centered upon a more complex underlying spectrum. If the alcohol contains deuterium in the hydroxyl position the line is sharper than if it contains hydrogen. Upon bleaching, the line disappears and the underlying complex spectrum becomes more intense. The underlying spectrum in ethanol, in general, is more complex than that for methanol because of the larger number of protons contained in the paramagnetic species. The manner in which the complex spectrum in ethanol varies with deuterium substitution shows that the paramagnetic species present after bleaching contains four of the five hydrogens originally present on the two carbon atoms and that the fifth hydrogen must have left the α-carbon. Radicals consistent with this include CH_3-CHOH and the ion radical (*8*) $C_2H_4^+$. It has not been possible to tell if the hydroxyl hydrogen is present or absent. Similarly in methanol the three lines in the bleached material originate from a species containing two of the three hydrogens originally present on the carbon, and it is not possible to make a definite statement about the presence or absence of the hydroxyl hydrogen. The presence of the radical CH_2OH is supported by the finding of glycol as a final product (*9*).

The precursor species presumably does contain the hydroxyl hydrogen. The broader line when hydrogen rather than deuterium is present in the hydroxyl position is likely caused by an unresolved hyperfine splitting. The size of the deuterium hyperfine splitting is so small compared to the line widths that its effect is simply to block its position from showing hyperfine effects. The nature of the precursor species is subject to speculation. It could, for example, be the alcohol ion, i.e., CH_3OH^+ or $C_2H_5OH^+$. The various experiments, especially on ethanol, show more complexity than can be discussed here. The discussion does, however, indicate the type of detailed information that is now being obtained by paramagnetic resonance.

Single Crystals

As indicated earlier, the g value of a free electron spin is 2.0023. An unpaired electron in a paramag-

netic species may have orbital motion that gives rise to a magnetic moment which can, in general, cause the g value to depart from the "spin only" value. Many radiation-produced species in solids do have g values near 2. The large, stable organic free radicals as solids also have g values very close to the free electron value. This is a consequence of the rather complete quenching by intra and/or intermolecular interactions of the magnetic moment associated with the orbital motion of the unpaired electron. Nonetheless, some orbital effects frequently persist. One effect caused in crystalline solids is for the g value to have different values depending upon the way the applied magnetic field is oriented with respect to the crystal axes. This means that single crystals should be used for most meaningful results. Polycrystalline samples would have spectra that are broadened by this anisotropy. Similarly, the hyperfine splittings may show anisotropy. Thus different spacings of hyperfine lines would be found for different orientations of the single crystal in the magnetic field. A detailed study of single crystals gives most significant results. Great care must be exercised in interpreting results from powdered or glassy materials to make sure effects of anisotropy are not obscuring important features of the spectrum. Atomic hydrogen is a particularly favorable case for study even in glassy or polycrystalline samples since the unpaired electron is an s electron and, hence, has no orbital magnetic moment. Other species formed in the irradiated acids, however, should best be studied with single crystals. For example, a study (*10*) of single crystals of $H_2SO_4 \cdot H_2O$ and $H_2SO_4 \cdot 2H_2O$ has shown the broad line of Figure 1 to be made up of a large number of smeared out sharper lines. At least two different species contribute to the family of sharper lines that were observed.

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Radiation Chemistry of High Polymers

Among the many possible systems which may be selected for a study of the interaction between radiations of high energy and matter none is more interesting than a system composed of one or more of the many synthetic high polymers which are now available. This is especially true for studies involving solids, because solid high polymers may be crystalline, amorphous, or glassy. Furthermore, certain specific radiation-sensitive groups may be chemically synthesized into the long polymer chains at known locations and the effect of both chemical type and location on the radiation effects studied. An example of this is the interesting work done by Alexander and Charlesby (*1*) on copolymers of styrene and isobutylene in which they showed that some of the energy absorbed by the isobutylene must be transferred to the styrene segments, thus deactivating the isobutylene components before they could react. Alexander and Charlesby also found that the aromatic naphthalene ring substituted into the center of a C_{22} paraffin molecule had a greater effect in "protecting" the saturated hydrocarbon from the radiation than when substituted at the ends of the molecule.

The irradiation of solid high polymers also makes possible studies of free radicals as, under certain favorable conditions, they can be trapped in the solid. Their rate of reaction at different temperatures can be observed subsequently, and the kinetics and mechanism of their decay developed. This is a field of research that is just beginning.

It is quite easy to prepare most polymers in the form of thin films (*2*) whose infrared absorption spectra both before and after irradiation can be measured, and from the observed optical densities, changes in the concentrations of certain specific groups calculated. Furthermore, the film thickness is easily varied, so that the kinetic relationship can be developed between diffusion of gases, such as oxygen, in the polymer and chemical reaction of the polymers with the dissolved gas during the irradiation.

The irradiation of polymers has practical as well as theoretical interest. The crosslinking of polyethylene by high energy irradiation increases form stability and

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resistance to flow at temperatures above the melting point. Therefore it is profitable to irradiate polyethylene film with high energy electrons. The General Electric Company is now doing this and is marketing the irradiated polyethylene under the trade name "Irrathene." As far as the author is aware, this is the first example of commercial improvement of materials by high energy radiations.

Before describing in detail the chemical effects of the radiation on high polymers it should be pointed out that the magnitude of the dose required to produce significant results is enormous compared to the dose level about which one must be concerned in avoiding deleterious physiological effects in the human body. Thus, it is now believed that a person should not accumulate more than 100 roentgens of radiation during his lifetime, yet a million or more roentgens must be absorbed by polyethylene before observable changes in unsaturation, crosslinking, vinyl-group decay, etc., occur.

Crosslinking

Perhaps the most remarkable and most unexpected result of the radiation of polyethylene is the formation of cross-links. This beneficial effect was not expected; rather deleterious degradation was the confident prediction. The effect is remarkable because it involves at room temperature and without chemical catalysts or activators the formation of C—C bonds between chains of a saturated hydrocarbon. The first clue (*2*, *3*) to crosslinking by irradiation came from stress-strain measurements on thin strips of polyethylene film irradiated in vacuum in the heavy water pile of the Argonne National Laboratory (see Fig. 1).

Later Charlesby (*4–13*) and co-workers at the United Kingdom Atomic Energy Research Establishment at Harwell, near Oxford, England, made many important radiation studies on polyethylene and other polymers. In particular Charlesby (*4*) found that irradiated polyethylene became partly insoluble, and acquired the properties of a three-dimensional network gel. Figure 2 illustrates some of Charlesby's results for the ultimate tensile strength of polyethylene at different temperatures as a function of dose (*42*). The lowest curve is especially interesting as it demonstrates the great increase in tensile strength for irradiated polyethylene at elevated temperatures.

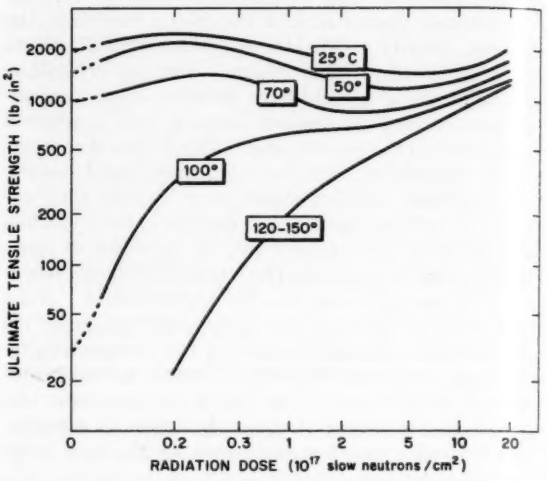


Figure 2. Ultimate tensile strength of irradiated polyethylene. Data of Charlesby (*42*). Figure reproduced by kind permission of Professor Charlesby and *Nucleonics*.

Figure 3 illustrates a typical example (*33*) of the growth of insolubility of a linear, highly crystalline

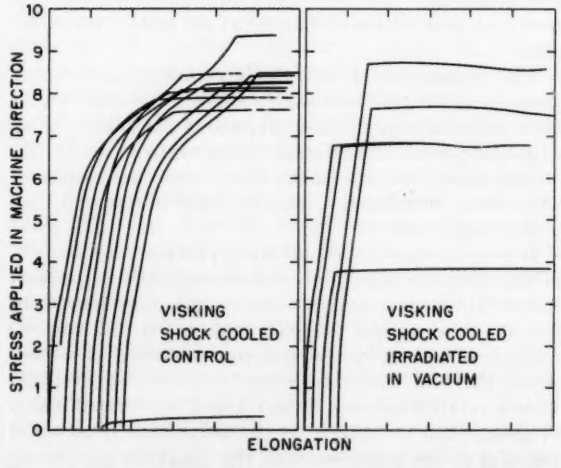


Figure 1. Stress-strain curves for unirradiated (*left*) and irradiated (*right*) low density polyethylene. Each curve represents data for a single strip of film elongated at a constant rate of loading until break (indicated by sharp break in curves). "Machine direction" means direction in which film was extruded during formation. "Shock cooled" means rapidly quenched film.

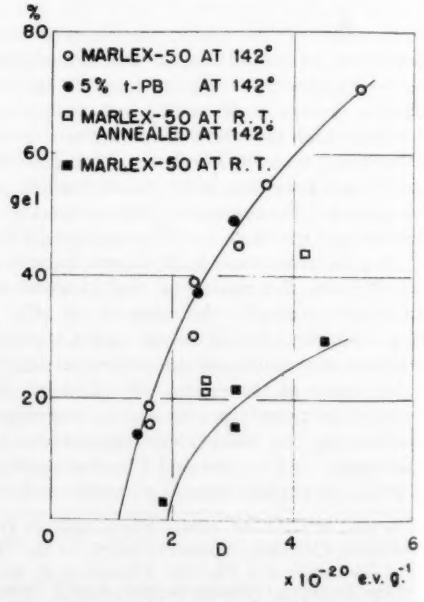


Figure 3. Formation of insoluble gel in polyethylene as a function of dose. The dose at the gel point is indicated by the intercepts on the abscissa.

polyethylene, Marlex-50, as a function of the dose of gamma rays from a cobalt-60 source. It is interesting to note that the insolubility increases faster with dose than at room temperature if the irradiation is carried out at 142°C above the maximum melting point of the polymer. Furthermore, if the material is irradiated at room temperature and then annealed to 142° subsequent to the irradiation, the insolubility is greater than it would be without the annealing as can be seen also from Figure 3. This interesting phenomenon, which would be even more pronounced if the solubility measurements could be made at room temperature instead of at 110°, the boiling point of the solvent, toluene, is further chemical evidence for the existence and persistence of trapped free radicals in the polymer subsequent to the irradiation. Trapped free radicals[1] created by the irradiation of polymers were first shown to persist at room temperature by Sears and Parkinson (*14*) who observed a post-irradiation growth of the carbonyl absorption band in the infrared at 5.9 μ. This observation of post-irradiation oxidation has been confirmed for Marlex-50 polyethylene by Lawton, Balwit and Powell (*15*, *16*) and by ourselves (*17*). Electron spin resonance studies by Lawton, Powell, and Balwit (*16*) have shown the rate of decay of trapped free radi-

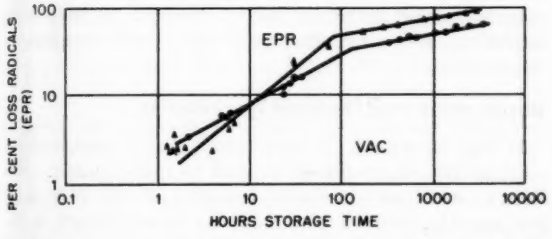


Figure 4. Decay of trapped free radicals in vacuum subsequent to the irradiation. Data of Lawton, Powell and Balwit (16) reproduced by kind permission of Dr. Lawton.

cals at room temperature. A typical curve for free radical decay is shown in Figure 4. According to studies at liquid nitrogen temperature by Smaller and Matheson (*18*) the radicals persisting in greatest abundance were

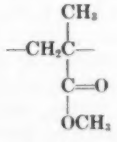
$$-CH_2\dot{C}HCH_2-$$

If the viscosity of solutions of the soluble fraction of irradiated polyethylene is measured (*19*, *20*) the viscosity increment per gram due to the polyethylene at first rises until the gel point is reached, and then falls. The gel point is defined as the moment during the irradiation when an insoluble gel structure can be first detected. The maximum in the viscosity-dose curve for the soluble fraction is one measure of the gel point. The decrease of viscosity beyond the gel point is due to the parallel decrease in the average molecular weight of the soluble fraction. Since the crosslinking occurs with a higher degree of probability between molecules of greatest molecular weight, which then become insoluble as an infinite network is formed, it can be understood why the resultant average molecular weight of the soluble fraction, and with it the viscosity increment, decreases as the dose increases beyond the gel point. All of this behavior is in accord with the statistical theories of gelation developed by Flory (*21*), Stockmayer (*22*), and Charlesby (*9*, *12*).

It is interesting to consider the effect of crosslinking on the melting point, the crystallinity of the polyethylene, and on the ability of molten polyethylene to crystallize. Dole and Howard (*23*) demonstrated that the thermodynamic maximum melting point of the polyethylene decreased only slightly with irradiation while the crystallinity was hardly affected unless one exposed the polyethylene to very high doses. On the other hand, Woodward, Deeley, Kline, and Sauer (*24*) observed that the dynamic modulus of irradiated polyethylene as measured at 20° decreased due to a post-irradiation melting and recrystallization. They correctly interpreted this latter fact on the postulate of inhibition of crystallization due to cross-links. Thus on melting a highly crystalline but irradiated polyethylene, and recooling to room temperature, crystallization to the original high extent was inhibited, presumably by the cross-links. Inasmuch as amorphous polyethylene absorbs in the infrared at 1080 and 1303 cm^{-1} whereas crystalline polyethylene does not, Williams, Matsuo, and Dole (*32*, *49*) were able to confirm by direct measurement of the amorphous content the hypothesis of inhibition of crystallization due to cross-links. For a quantitative interpretation of the data, account also had to be taken of end-link formation, i.e., the postulated reaction of an activated vinyl group with a neighboring methylene group of the polymeric chain. Both end-links and cross-links were assumed to inhibit crystallization by producing chain entanglements.

Degradation

If a polymer is degraded by the radiation instead of being cross-linked, the average molecular weight, of course, decreases. Polymethyl methacrylate, whose repeating structure is



is a good example of a polymer that apparently degrades on irradiation without crosslinking (*10*). Charlesby (*25*) states that the viscosity-average molecular, M_v, is given by the equation

$$M_v = \frac{K}{D_0 + D} \qquad (1)$$

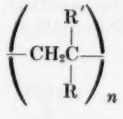
where K is a constant, D the dose and D_0 is "a small correction factor that can be considered as the 'virtual' radiation dose needed to produce the initial molecular weight from an infinite chain." Both the side chain and the main chain are believed to undergo degradation in a one to one ratio during the irradiation. The gases released during the irradiation are trapped in the solid causing the latter to crack on long exposures to the radiation. If a lightly irradiated sample is heated to about 120°, bubbles of gas form within the solid and the solid swells. In this way a solid foam can be produced.

[1] Schneider, Day, and Stein, *Nature*, **168**, 645 (1951) observed paramagnetic resonance in polystyrene and polymethylmethacrylate irradiated with X-rays, but attributed their observations to trapped electrons.

If the polymer cross-links partially, and is partially degraded, it is very difficult to determine the relative extents of crosslinking and degradation. Charlesby (*26*) has derived equations for the percentage of gel as a function of dose in the case of polymers having initially a random molecular weight distribution and undergoing random chain scission due to the irradiation. In the case of polyethylene, however, the molecular weight distribution is not random initially, the weight to number average molecular weight ratio being as large as 10 or more. For a random distribution, the ratio should be two. At the moment there is considerable uncertainty regarding the extent of chain scission in polyethylene due to the high energy radiations. It appears to be small and is usually neglected, especially for irradiations in vacuum. The rupture of C—C bonds on the hydrocarbon side chains of branched polyethylenes cannot be overlooked, however. Dole, Keeling, and Rose (*19*) estimated that the rupture of C—C bonds in side chains was about half as frequent as C—H bond rupture. They could find no evidence for rupture of C—C bonds along the main chain. This view that the C—C bond rupture is mainly C—C bonds of side chains has been confirmed by studies of branch-free linear polyethylene when the gases evolved by the irradiation contain practically no hydrocarbons. This proves that the hydrocarbon gases observed by Dole, Keeling, and Rose must have come from the rupture of side chains.

Comparison of Polymers that Degrade or Cross-link

It is interesting to attempt to classify polymers into two groups, those that predominantly cross-link on irradiation and those that undergo chain scission. This subject has been reviewed by Bovey (*27*). Miller, Lawton, and Balwit (*28*) pointed out that vinyl polymers which predominantly degrade during irradiation have the structure



This is reasonable inasmuch as double bond formation by the radiolytic evolution of hydrogen atoms from neighboring carbon atoms cannot occur. (Double bond formation is considered later.) Furthermore, the side groups probably interfere sterically with C—C bond formation between neighboring chains. It is essential, of course, that carbon atoms approach each other to a distance of the order of 1.54 Å for C—C bond formation to occur. The extent to which chemical reactions occur ensuant upon the absorption of the relatively great energy of the incident gamma rays via the intermediaries, the Compton electons, depends, when competing processes exist, on their relative rapidity. To understand chain scission as opposed to crosslinking one should write down all possible reactions and then attempt to find the one reaction that will occur more rapidly than any other. Wall (*29*) has correlated the resistance of the polymer chain to scission with the heat of polymerization of the monomer. Thus polymers formed from ethylene, propylene, methyl acrylate, acrylic acid, and styrene all have heats of polymerization greater than 16 kcal/mole and cross-link, while methacrylic acid, isobutylene, methyl methacrylate, and α-methyl styrene have heats of polymerization less than 16 kcal/mole and undergo scission. Wall thus uses the heats of polymerization as a measure of the stability of the C—C bond in the polymer. Bond energies (*30*) do not always correlate with radiation stability as the C—H bond strength (4.08 ev) is considerably greater than that of the C—C bond (3.21 ev) yet it is the C—H bond that is predominantly ruptured in the case of polyethylene. More correctly it probably should be said that the C—C bond reforms more rapidly after rupture than the C—H bond inasmuch as the cage effect should be much more important for C—C recombination than C—H. One can imagine in the first place the two long fragments of the broken hydrocarbon chain being held nearly rigidly in position until recombination occurs, and in the second place the extremely mobile H atom or molecule rapidly diffusing out of the localized region of ionization and excitation, and, consequently, becoming unavailable for recombination.

Some other polymers that cross-link are the polysiloxanes, natural and various synthetic rubbers, chlorinated polyethylene, etc.; additional polymers that suffer degradation are cellulose and other oxygen containing polymers, polymers containing halogens such as polyvinyl chloride (this is said to cross-link as well as to degrade), polyvinylidene chloride, polytetrafluoroethylene, etc.

Unsaturation and Chemical Mechanisms

It was shown (*2*, *3*) very early that *trans*-vinylene unsaturation is produced as well as crosslinking. To form a cross-link or a double bond a molecule of hydrogen must be evolved, and this was indeed found to be the case (*2*, *3*, *19*). The gas evolved in the case of the irradiation of a linear polyethylene was found (*31*) to be over 99% hydrogen. However, quantitative agreement between the sum of cross-links and double bonds formed and molecules of hydrogen liberated has yet to be achieved satisfactorily. Difficulties are (1) unambiguous determination of the yield of cross-links, (2) the impossibility as yet of measuring the number of intramolecular C—C bonds produced in forming cyclic compounds, (3) determination of the number of free radicals persisting after the radiation, (4) determination of number of hydrogen molecules "lost" by a possible back reaction, (5) uncertainties involving effect of decay of initial unsaturation in producing gel structures. Space does not permit a detailed discussion of all of these points. Dole, Milner, and Williams (*31*) interpreted a new infrared absorption band which appeared at 10.1 μ during the irradiation of Marlex-50 polyethylene as due to cyclic structures, "ring-links." This effect was not observed for radiations in the liquid state. Similarly, free radicals probably do not persist in the liquid; hence liquid irradiations should be theoretically simpler to interpret than the irradiations of solid polymers. Arvia and Dole (*32*) found a reduction in $G(H_2)$ (molecules of hydrogen evolved per 100 ev of energy absorbed) with increase of ambient hydrogen pressure in the case of Marlex-50 polyethylene irradiated at room temperature. They attributed this to a back reaction involving molecular hydrogen.

The fifth difficulty of attaining a quantitative ma-

terial balance in the irradiation of polyethylene listed above relates to the decay of unsaturation. All polyethylenes initially contain varying amounts of different types of unsaturation; thus the unsaturation in Marlex-50 is vinyl unsaturation, in low density polyethylenes predominantly vinylidene, in Standard Oil (Indiana) polyethylene, *trans*-vinylene and in a Ziegler polyethylene, vinyl, vinylidene, and *trans*-vinylene. The concentration of these groups in polyethylene is most conveniently estimated from infrared absorption spectra taken on polyethylene films. All types of double bonds disappear on irradiation including those produced by the radiation. In the case of the latter a balance is eventually attained between the rate of production and the rate of decay. The kinetics of the radiolytic formation and decay of the double bonds has been studied by Dole, Milner, and Williams (*31*), and Williams and Dole (*33*). In general it can be said that the growth is zero order and the decay first order. The only type of double bond produced to a significant extent by the irradiation is *trans*-vinylene. Its growth and decay in Marlex-50 and other polyethylenes is accurately described by the equation

$$\frac{[\mathrm{Vl}] - [\mathrm{Vl}]_0}{[\mathrm{Vl}]_\infty - [\mathrm{Vl}]_0} = 1 - e^{-k_2 D} \qquad (2)$$

where [Vl], D and k_2 represent the *trans*-vinylene concentration, the dose and the first order vinylene decay constant, respectively. The subscripts zero and infinity refer to the extent of the dose. Figure 5 illustrates

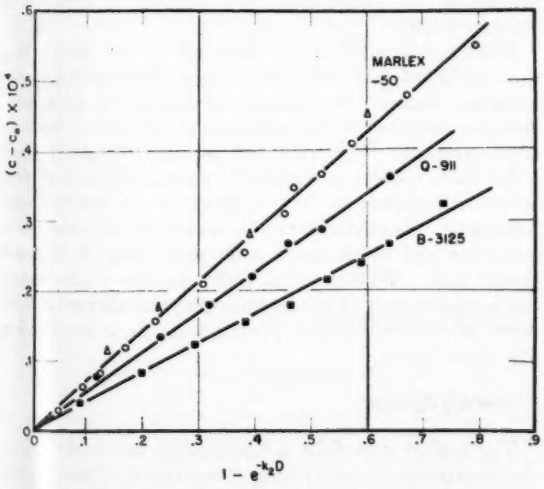


Figure 5. Test of equation (2) for zero order growth and first order decay of *trans*-vinylene unsaturation. The middle curve represents data for a Ziegler type polyethylene and the lowest curve for a low density polyethylene. Marlex-50 is a linear, high density polyethylene.

the applicability of equation (2) to three polyethylenes, Marlex-50, a Ziegler polyethylene, and a low density polyethylene.

Energy Transfer in Polymers

A fascinating problem is concerned with the mechanism by which the energy of the highly energetic incident gamma rays is distributed and dissipated within the polymer. First of all, it should be pointed out that most of the energy is degraded to heat inasmuch as the net (minimum) energy required to produce the observed chemical effects in polyethylene is less than 5% of the total energy absorbed. Thus, the production of chemical effects by radiation is very inefficient unless the radiation can be used to initiate chain reactions. An example of the latter is the initiation of polymerization of vinyl monomers due to the free radicals created by the radiation.

In the case of a low density polyethylene it was early observed (*19*) that vinylidene unsaturation disappeared about 300 times more rapidly relative to hydrogen evolution on irradiation than one would calculate statistically (*34*). The decay of vinyl unsaturation (*35*) in Marlex-50 polyethylene follows a similar nonrandom pattern. When the gamma ray passes through the polyethylene, so-called Compton electrons are knocked out of their normal energy states in the polyethylene molecule. This electron next causes the ejection of other electrons, i.e., the formation of ion pairs, in a region close to the location of the first electron. It is believed that each localized region of ionization absorbs about 100 ev of the gamma radiation, that the regions of ionization, called "spurs" are about 1000 Å apart, and that 3 to 4 ion pairs are produced in each spur. As the energy of ionization of a saturated hydrocarbon is probably about 10 ev, 60 to 70% of the absorbed energy first appears as energy of excitation.

Dole, Milner, and Williams (*31*) have postulated that this energy of excitation is rapidly transferred to vinyl groups, probably throughout a sphere of about 36 Å in radius. However, when sufficient vinylene unsaturation has been created in the polyethylene at random sites by the irradiation, the rate of decay of vinyl groups in Marlex-50 at room temperature fails to follow the first order law. The explanation of this phenomenon, which is limited to the solid state, is that the vinylene groups "protect" the vinyl groups from receiving as much excitation energy as they would if the vinylene groups were not present. In the liquid state a protective action can be produced by dissolving *trans*-1,4-poly(butadiene) in the Marlex-50. In this case both the hydrogen evolution and vinyl decay are reduced by the presence of the polybutadiene. As the polybutadiene has very little effect when the liquid mixture is solidified and the polybutadiene becomes segregated into the amorphous regions, it appears that a random and uniform distribution is necessary for the most efficient energy transfer.

Radiolytic Oxidation

The oxidation of polyethylene due to the activating influence of high energy radiations was first observed by Rose and Dole (*2*, *3*) who concluded that oxidation was largely a surface effect. They found by chemical analysis that thick granules of polyethylene gained a smaller percentage of oxygen than films when films and granules were simultaneously irradiated. Charlesby (*4*) also noted the surface oxidation.

Magat (*36*, *37*) and Chapiro (*38*) and their co-workers have studied the radiolytic oxidation of polyethylene and have used the peroxides formed on the surface to initiate vinyl polymerization. If the radiolytically and surface-oxidized polyethylene is heated, the peroxides dissociate to free radicals which initiate the polymerization. Some of the vinyl monomers which polymerize

are bound chemically to the polyethylene. Henglein, Schnabel, and Heine (*39*) have used gamma radiation to produce both surface and bulk grafting of one polymer to another. In this case the monomer is allowed to diffuse into a polymer of different type and then the system is exposed to the gamma radiation. The result is a surface graft or a bulk graft depending on how far the monomer had diffused into the polymer. This process is not one of oxidation, but is mentioned here because of its relation to the processes of Magat and Chapiro.

Matsuo and Dole (*40*) have made a study of the kinetics of the radiolytic oxidation of thin films of antioxidant free Marlex-50. If the intensity of the gamma radiation is high enough, a steady state balance between the oxygen diffusing into the film and the oxygen reacting with the free radicals is soon established. If the film is thick enough, the concentration of dissolved oxygen at the center of the film drops to zero; in other words, the oxygen is consumed so fast as it penetrates into the film that it is all "cleaned-up" before reaching the middle of the film. Matsuo and Dole estimated that the thickness of a film above which no further oxidation could be detected under their experimental conditions (6 cm O_2 pressure, room temperature, radiation intensity about 0.2 mr per hour) was 0.05 cm.

Gas analysis of the radiolytic gaseous oxidation products and infrared analysis of the radiolytically oxidized film showed that carbonyl formation was a linear function of the oxygen consumed, irrespective of whether the oxygen reacted with the film during the irradiation or subsequent to it (dark reaction with trapped free radicals). Water production and carbonyl formation were also linearly proportional to each other. Some carbon monoxide, about an equal amount of carbon dioxide, and traces of acetone and methyl alcohol were formed.

Among various possible oxidation mechanisms that can be postulated, the following seems to be the most reasonable in the light of the evidence obtained by us and many others (*41*).

$$2RH \xrightarrow{\sim\sim} 2R\cdot + H_2 \qquad (3)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (4)$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \qquad (5)$$

$$RR'CHO_2\cdot \rightarrow R\dot{C}R' \quad (\dot{C}R' = \text{OOH}) \qquad (6)$$

$$R\dot{C}R' \rightarrow RCR' + OH\cdot \quad (\dot{C}R' = \text{OOH};\ CR' = \text{O}) \qquad (7)$$

$$OH\cdot + RH \rightarrow R\cdot + H_2O \qquad (8)$$

$$2ROO\cdot \rightarrow O_2 + RCR + RCHR \quad (CR' = \text{O};\ CHR' = \text{OH}) \qquad (9)$$

$$R\cdot + ROO\cdot \rightarrow ROOR \qquad (10)$$

In this scheme reaction (3) represents the initial formation of free radicals by the absorbed radiation. Reactions (4) and (5) constitute a chain, and (9) and (10) are termination reactions. The carbon monoxide and carbon dioxide probably come from the decomposition of acids or from chain scission. Water may come from the decomposition of hydroperoxides or from reaction (8).

When Marlex-50 polyethylene is irradiated in a vacuum at room temperature (there is an enhanced effect at liquid nitrogen temperature) and then exposed to oxygen of the air, a slow oxygen uptake will proceed for days. The post-irradiation oxidation effect was first discovered in the case of polystyrene by Sears and Parkinson (*14*); later, it was also noted to occur in the case of Marlex-50 (*15–17*). The reaction mechanisms have not been worked out, but there is no reason to believe that the reactions are different from those listed above. The work of Magat (*36*) and Chapiro (*38*) demonstrates rather conclusively that both peroxides, stable to about 150°, and hydroperoxides, stable perhaps only to room temperature, are formed in the radiolytic oxidation. It should be noted that if polyethylene, irradiated in a vacuum, is annealed to 142° before exposure to air, the post-irradiation oxidation with its concomitant deleterious effect is eliminated.

Other Radiation Effects

Space does not permit an extensive discussion of other interesting radiolytic effects. Among these are effect of the radiations on mechanical properties (*42*), nuclear magnetic resonance spectra (*43, 47*), electrical conductivity (*44*), permeability (*45, 46*), etc. In some as yet quite preliminary work, Fallgatter and Dole (*48*) have demonstrated a significant increase in solubility of hydrogen gas in polyethylene on irradiation. This may be due to the production of solid defects (*43*) as annealing seems to reduce the enhanced solubility although at the same time the amorphous content is increased (*49*).

Finally, reference should be made to the interesting work of Golub (*50*) who has studied the kinetics of the radiation induced *cis-trans* isomerization of polybutadiene in solution in the presence of sensitizer such as allyl bromide. The reaction is approximately half order with respect to bromide concentration and first order with respect to the concentration of the *cis*-polybutadiene. Isomerization also occurs in the absence of sensitizer and in the pure solid state, but at a much slower rate. Williams and Dole (*34*) have also noted the isomerization of *cis* to *trans*-polybutadiene in mixtures of Marlex-50 and *cis*-polybutadiene containing 5% of the latter.

Acknowledgment

The author gratefully acknowledges the early financial assistance of the Visking Company of Chicago, the initial cooperation of the technical staff of the Argonne National Laboratories, the present support of the U. S. Atomic Energy Commission, and the gift of materials from the Phillips Petroleum Company, Hercules Powder Company, E. I. du Pont de Nemours and Company, Dow Chemical Company, United States Rubber Company, and the Standard Oil Company (Indiana). To his co-workers D. G. Rose, C. D. Keeling, W. H. Howard, D. C. Milner, A. J. Arvia, T. F. Williams, H. Matsuo, T. Buch, and M. Fallgatter he wishes to express his never ending appreciation for their assistance and original contributions.

The final paper in this symposium, "Radiation Effects of Solids" by E. H. Taylor, will appear in the August issue.

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[1] See *C & E News*, May 25, 1959, p. 26.

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

Chemical Education in the Union of South Africa

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P.O. Box 1037
Stanford, California

A steady stream of chemical educators, and chemists in general, moves to Europe, but only a trickle finds its way to other parts of the world. In an area such as South Africa this trickle has slowed down to a not-too-constant dropwise rate. For this reason we face a rather deplorable lack of knowledge as far as both chemical education and general chemical development are concerned. This paper will endeavor to alleviate this situation by looking into the first-mentioned point. With the realization that they face problems similar to ours, possibly we can benefit from the experience of the South African chemical educators and their approach to the solution of problems in chemical education.

University Students

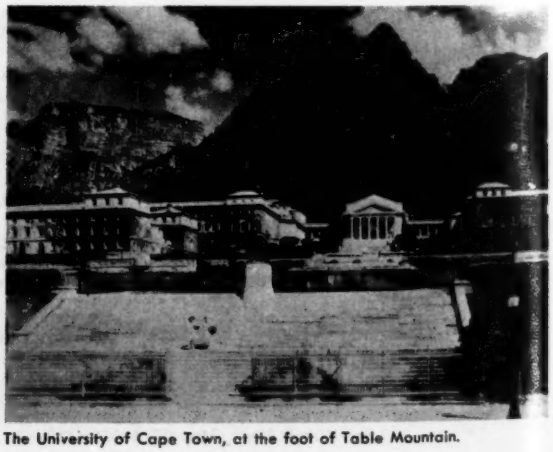
The university education is patterned after the British system. A high school student, after passing his final examination, which is given on a Union-wide basis, may attend a university, usually of his choice. However, some universities have had to be selective in admitting students, due to lack of facilities and funds. This tightening of admission policy also ties in with the complaint that high schools do not turn out high caliber graduates. Much time must be spent in teaching them fundamentals. Since a B.Sc. degree in chemistry may be obtained after only three years, this lack of basic knowledge presents a definite problem. Furthermore, in spite of admonitions from the chemistry teaching staffs, the curriculum at some universities allows the students too much leeway in selecting courses. However, the so-called Honors Degree, generally a prerequisite for graduate work, requires four years of undergraduate study, with the fourth years consisting of advanced course work, and some research. Most faculties feel that students who may not have high grades might turn out to be excellent research workers. Honors year research helps the faculty to evaluate the research potential of the prospective graduate student. The M.Sc. degree is considered a stepping stone toward the Ph.D. degree, and the trend seems to be to make a master's degree mandatory prior to admittance to candidacy for a doctor's degree. It is felt that this additional requirement will greatly increase the probability that only students who are well qualified will embark on the Ph.D. curriculum. Furthermore, those students who fail to attain the high standards required of a doctoral candidate will be eliminated at an early stage. Thus, neither too much of their time nor that of the faculty will be wasted. Each doctoral dissertation has to be passed on by an external examiner who may, if he feels justified, reject a dissertation, as not coming up to standard. If both he and the university committee accept a dissertation, the candidate has qualified for his degree. In order to set more definite, and generally higher, standards some faculty members have proposed the setting up of a central board to pass on dissertations.

The Role of the Graduate

Assistantships and fellowships go begging, because the student with a bachelor's degree has no desire to go into graduate school. Several reasons cause him to make this decision. Industry, with a few exceptions, shows as yet no interest in research, and training for it. A person with a bachelor's degree finds no trouble in securing a well-paying position. Even students who fail, and in one university 30% of one class failed their second year examinations, are approached by company representatives and hired. Consider the much tougher road a Ph.D. candidate must face. After several years of low-income, although rewarding, work he receives his degree. Since most industry considers him less desirable than a graduate with a B.Sc. degree, he will find only limited demand for his talents. Government laboratories offer opportunities to some, with relatively poor pay.

University Faculties

Good teaching positions, with only eight universities in the country, cannot be found easily, and are not



The University of Cape Town, at the foot of Table Mountain.

remunerative. In a system which calls for one professor for each departmental division only, advancement transitions do not take place often. The relatively young and healthy holder of a chair may drive to despair the younger faculty members. Two approaches try to correct the situation. In certain cases, the more enlightened industries have given financial aid to the more promising young staff members. Some universities, going by American precedent, have made isolated appointments in special cases to associate professors. Yet, with teaching loads up to 16 hours per week, correcting of examinations a mandatory faculty function, time for research being limited, the hiring and retaining of qualified instructors proves difficult. Whereas formerly the United Kingdom, as well as the continent, to a smaller degree, used to supply personnel, this source seems to have dried up. Some universities decided to sacrifice quality in order to fill the ranks of the faculty; others decided to go without the number of instructors required rather than appoint less qualified persons. Nevertheless, many faculty members excel in teaching and research.

Some novel approaches in presenting chemistry may be cited. At Cape Town Professor F. G. Holliman takes a new look at the teaching of organic chemistry by avoiding a breakdown into aliphatic and aromatic chemistry but rather basing his course on a functional group approach, with a definite physical-organic influence. A long-needed rewriting of the presentation of physical chemistry is being undertaken by Dr. V. Pretorius, at the University of Pretoria. His discussion begins with a survey of elemental particles; from here he expands into the various fields of physical chemistry, tying them all together by means of the elemental particles approach.

Student-Faculty Relations

A somewhat more formal relationship seems to exist between students, both undergraduate and graduate, and faculty than may be found at our colleges and universities. But since teaching takes precedence over research in the Union universities, the faculty member dedicates more time to his students than his counterpart at many of our universities. Taking advantage of an open-door policy, a student may consult with an instructor any time he so desires. A twice daily "tea hour" seems to benefit graduate students greatly. It gives them an opportunity to get together with the faculty and discuss various problems regarding research, courses, or anything else of interest to them. Some of the staff who have visited our institutes of higher learning stated that they missed this type of meeting, with its pleasant, informal, and stimulating exchange of ideas.

Research

In spite of the heavy teaching load, the universities manage to turn out respectable research. It covers many fields of chemistry, with special interest shown to the natural products field. Several research institutes exist, supported by the government and, to some extent, by the industries concerned. The largest organization is the Council for Scientific and Industrial Research, CSIR, with headquarters located in a campus-like area near Pretoria and smaller units all over the country. Although mostly applied research is carried out, it is hoped that once the personnel problem has found a solution, about 30% of the time may be allocated to investigations of a fundamental nature. Both basic and applied research contributed to the solution of one problem, the desalting of mine waters by means of an electrodialysis system which can handle three million barrels per day. The Leather Research Institute in Grahamstown, in addition to work on tanning processes, also does work in protein chemistry and the structure of tannin. A neighboring unit is the Wool Research Institute, primarily interested in results of value to wool growers, but hoping to start some long-range protein research. Similar problems are faced by the Fisheries Research Institute in Cape Town, doing routine analytical and developmental work for the fishing industry but hoping to start some long-term research programs. The same may be said of the Sugar Milling Research Institute in Durban. A Wine Research Group in Stellenbosch is getting started, and a Wattle Timber Research Institute in Pietermaritzburg looks into possible uses for wattle timber.

Academic Relations Between Universities, Industry, and Government

Research work done at CSIR, the national steel works laboratories, ISCOR, and at the research department of the African Explosives and Chemical Industries, Ltd., may count toward a degree. Higher degrees may be conferred on qualified persons by a local university or by the University of South Africa. This organization has its own faculty members and operates on a Union-wide basis. It also acts like a correspondence school and extension center. Selected industries give research grants, and African Explosives has an arrangement with a university whereby members of the company's research division will give lectures at the university, each person covering his major field of interest. Although this plan was designed to alleviate the lack of regular instructors, it may develop into a permanent addition to the curriculum.

Chemistry Instruction in Related Fields

A student desiring to take up medicine or dentistry enters the school of his choice immediately upon graduation from high school. After six years, an M.B. B.Ch.—medical bachelor and surgery bachelor degree—may be awarded. Original research is required for an M.D. degree, and requires two additional years of university. Knowledge of chemistry is required, but not emphasized.

The training of a pharmacist consists of two years in a technical college, roughly equivalent to our junior college, plus three years of apprenticeship in a pharmacy. A newly inaugurated alternative consists of a three-year university course, with a two-year apprenticeship. In either case the candidate must pass a national examination before obtaining a diploma and becoming a member of the pharmaceutical profession. The standards set by the State of California, as depicted in university course requirements, demand a more thorough foundation in chemistry.

Educational Exchange

Due, to some extent, to financial and currency considerations the great majority of scientific personnel in the Union receive their degrees either in their own country or the United Kingdom. Hope has been expressed that more of the promising students will attend universities in this country. Many chemists, authorities in their fields, regularly visit the United States, some for consultations, others for advanced studies, as do members of the medical profession. So far, not enough thought has been given to reciprocation.

Some American textbooks are used, especially in the field of chemical engineering. They so far excel in quality that the high price constitutes no major obstacle. This criterion does not apply to chemicals, or laboratory equipment. More and more, European makes are bought because of lower prices, generally equal quality, and better service.

A desire has been voiced for closer contact with the AMERICAN CHEMICAL SOCIETY and the AMERICAN INSTITUTE OF CHEMICAL ENGINEERS. This may lead to a profitable exchange of ideas.

Acknowledgments

The author takes great pleasure in expressing his gratitude to the many chemists, both in education and industry, for their hospitality and readiness to discuss their views.

Chem Ed

LETTERS

To the Editor:

We find it hard to believe that Sienko and Plane would write that "hydrogen ions do not exist in basic solution" (J. CHEM. EDUC., **36**, 217 (1959)). In fact, a usually reliable source indicates that Sienko and Plane did *not* write that "hydrogen ions do not exist in basic solution." What Sienko and Plane *did* write is that "in basic solution, hydrogen ions do not exist in any appreciable concentration" (p. 218, line 5) and again "the original solution is basic and does not contain any appreciable concentration of hydrogen ions" (p. 218, line 18).

Is it true, as one uncharitable soul has suggested, that Mr. Yalman's fifth column is the work of a rival publisher?

CORNELL UNIVERSITY
ITHACA, NEW YORK

M. J. SIENKO
R. A. PLANE

Report of the New England Association of Chemistry Teachers

Official Business

Twenty-first Summer Conference Program

The following program has been announced for the Twenty-first Summer Conference of the New England Association of Chemistry Teachers to be held at the University of Connecticut, Storrs, August 17–22, 1959. The conference is open to all interested persons and their families. Inquiries should be addressed to the Conference Secretary, ROY J. GRITTER, Department of Chemistry, University of Connecticut.

Monday evening, Aug. 17. Samuel P. Massie, Fisk University, "The Visiting Scientist in Chemistry."

Tuesday, Aug. 18. Morning: R. Christian Anderson, Brookhaven National Laboratory, "What Brookhaven Does for You." Field H. Winslow, Bell Telephone Laboratories, "Trends in Polyethylene Research." *Afternoon:* William C. Orr, University of Connecticut, "Nuclear Chemistry Today." John DeFeo, University of Rhode Island, "Chemical Aspects of Open-Heart Surgery." *Evening:* Seward E. Beacom, The General Motors Technical Center, "Radiotracer Techniques in Electrodeposition Studies."

Wednesday, Aug. 19. Morning: Leon A. Greenberg, Yale Laboratory of Applied Biodynamics, "Alcohol and the Human Body." Juan C. Montermoso, Quartermaster Corps Research and Development Center, "Research into Extreme Performance Polymers." Charles J. Kensler, Boston School of Medicine, "Chemical Carcinogenesis." *Afternoon and evening:* Trips, picnic, and theater party.

Thursday, Aug. 20. Morning: Erich A. Taylor, Portsmouth Priory, "Quantitative Experiments in the Secondary School Laboratory." Donald B. Summers, Glassboro (N. J.) State College, "The Role of Laboratory in the Advanced Placement Program." *Afternoon:* Jay A. Young, King's College (Wilkes-Barre, Pa.), "Practice in Thinking (a laboratory course)." E. F. deVillafranco, Kent School, "Experiments Which Will Keep Them Interested." *Evening:* John Lebourveau, Yankee Atomic Electric Company, "Atomic Power Reactors."

Friday, Aug. 21. Morning: Robert Lusskin, The Trubek Laboratories, "The Art and Science of Perfumery." Karl Folkers, Merck, Sharp and Dohme Laboratories, "Discovery of Mevalonic Acid and Its Sequence." *Afternoon:* John Yudkin, Queen Elizabeth College (London, England), "Some Vitamin-Carbohydrate Interrelationships." Leo Safranski, E. I. du Pont de Nemours & Company, "Gas Chromatography." *Evening:* Chemical Education Films—A Preview.

EUGENE C. WINSLOW
UNIVERSITY OF RHODE ISLAND
Co-chairman for program

Chem Ed

BOOK REVIEWS

Quantitative Chemical Analysis

Gilbert H. Ayres, Professor of Chemistry, University of Texas. Harper & Brothers, New York, 1958. ix + 726 pp. 16.5 × 24 cm. $7.50.

In the preface to this book the author states his approach " . . . a course in quantitative analysis is foremost, a course in chemistry, . . . the successful pursuit of the subject requires an understanding of the chemical principles and reactions, as well as of the numerical relationships serving as the basis for calculations from the analytical data."

The author has followed the indicated path well and has presented a book which is clearly a course in chemistry as indicated by the number of ionic equations and chemical formulas presented, and is a study of the numerical relationships as indicated by the number of problems (approximately 400) included.

The book consists of five parts. Part I on Fundamental Principles consists of 15 chapters, 204 pages, covering scope and aims, the balance, mass action principles, reliability of measurements, separation methods, and precipitation phenomena. Part II on Gravimetric Methods consists of 10 chapters, 81 pages covering the chemistry and calculations of a number of different gravimetric methods. Part III on Titrimetric Methods consists of 11 chapters, 200 pages, covering measurements of volume, calculations of titrimetric analysis, neutralization theory, redox theory, and the chemistry of neutralization, redox, precipitation, and complexation titrations. Part IV on Introduction to Physicochemical Methods consists of 4 chapters, 78 pages, covering colorimetry and spectrophotometry, potentiometry, conductometry, and polarography. Part V called Experimental, 110 pages, contains the techniques of common laboratory operations and directions for all laboratory experiments with adequate notes to assist successful laboratory work. The appendixes consist of tables of solubility products, ionization constants, redox potentials, a section on the use of logarithms, and a section on suggestions to teachers. A 4 place logarithm table is included. The front cover contains International Atomic Weights and the back cover contains a table of frequently used formula weights.

While the reviewer has no fundamental disagreement with the material included in Part IV, it is his belief that the space spent on potentiometry, conductometry, and polarography might have been better used to expand some sections of greater importance to the beginning student in this area.

The book has been very carefully written and edited. The printing is good and the line diagrams in the text are excellent. There is no doubt that any student who is fortunate enough to have this as the assigned text should find that the explanations are thorough and understandable, and that the principles and methods covered in the book will be an excellent foundation for further study in chemistry.

RANDALL E. HAMM
University of Utah
Salt Lake City

Reviewed in this Issue

Gilbert H. Ayres, Quantitative Chemical Analysis
Joseph I. Routh, 20th Century Chemistry
James J. Lingane, Electroanalytical Chemistry
Nicholas D. Cheronis, James B. Parsons, and *Conrad E. Ronneberg*, The Study of the Physical World
Gmelins Handbuch der Anorganischen Chemie. System 45. Germanium Supplement
John R. Dillinger, Editor, Low Temperature Physics and Chemistry
H. Eyring, C. J. Christensen, and *H. S. Johnston*, Editors, Annual Review of Physical Chemistry. Volume 9
Herbert W. Cremer and *Trefor Davis*, Editors, Chemical Engineering Practice. Volume 4
J. B. Nielands and *Paul K. Stumpf*, Outlines of Enzyme Chemistry Reports of the Fourth Soviet Conference on Electrochemistry
Émile Monnin Chamot and *Clyde Walter Mason*, Handbook of Chemical Microscopy. Volume 1
W. Theilheimer, Synthetic Methods of Organic Chemistry. Volume 12
N. F. Mott and *H. Jones*, The Theory of the Properties of Metals and Alloys
R. Houwink, Elasticity, Plasticity, and Structure of Matter
Heinz Fischer and *Lawrence C. Mansur*, Editors, Conference on Extremely High Temperatures
L. J. Bellamy, The Infrared Spectra of Complex Molecules
F. D. Gunstone, An Introduction to the Chemistry of Fats and Fatty Acids
Arthur I. Vogel, Elementary Practical Organic Chemistry. Part 3
Clyde Orr, Jr., and *J. M. DallaValle*, Fine Particle Measurement
Irving Skeist, Epoxy Resins

20th Century Chemistry

Joseph I. Routh, Professor of Biochemistry, State University of Iowa. 2nd ed. W. B. Saunders Co., Philadelphia, 1958. xviii + 613 pp. 267 figs. 16 tables. 15 × 21 cm. $6.50.

The general nature of this volume is revealed in the beginning with the twelve-page table of contents where the author identifies his attempt to cover the fundamentals of general chemistry, of organic chemistry, and of biochemistry. The result is a book developed not with the chemistry major in mind but as an effort to interest the non-major in this field by telling him what chemistry is about.

Consequently, the descriptive historical approach is generally used. There are numerous pictures and diagrams throughout the book that emphasize the mechanics and uses of chemistry and its products. Very little stress is given to mathematics of chemistry; for example, only four problems on solutions and four on the gas laws. The old planetary concept with revolving electrons is used and there is almost no consideration of energy levels or the quantum mechanical view of atomic structure.

The majority of suggested references, the biochemistry section excepted, are from the literature of the 1930's and 1940's which reveal the author's interest in the type of general chemistry given during those years.

W. G. KESSEL
Indiana State Teachers College
Terre Haute

Electroanalytical Chemistry

James J. Lingane, Professor of Chemistry, Harvard University. 2nd ed., revised. Interscience Publishers, Inc., New York, 1958. xiii + 669 pp. Figs. and tables. 16.5 × 23.5 cm. $14.50.

It will be difficult to understand how anyone owning the earlier version of Professor Lingane's outstanding monograph will be able to resist this second edition. The material which made the first volume invaluable to students and teachers of modern analytical chemistry is still present and well revised. In addition, the present book is truly enlarged and the new topics are treated in a thorough and comprehensive manner. It is hardly fair to call it a second edition—this is a new book and one which should be on every analytical chemist's shelf. In fact, quite a wide variety of chemists, student and graduate, could profit from Lingane's lucid and forthright interpretation of the emf of galvanic cells, controlled potential methodology, etc.

Among the new material, Chapter 2 on common electrical measurements is a welcome addition. Straightforward and simple in approach, it nevertheless serves well as a background for those interested in the experimental techniques of electroanalytical work. The section on polarography fits its intended purpose as an introduction to the cardinal principles of this subject. The chapter on amper-

ometry is no mere introduction, but a critical treatment of the theory and applications with emphasis on interpretation through current-voltage curves.

In addition to an excellent presentation of the theory of coulometric titrations at constant current in Chapter 20, the chapter following contains perhaps the most complete and up-to-date discussion of applications yet available. Each coulometric titration is discussed in detail and evaluations of errors, scope of method, best operating techniques, etc., are to be found in many cases.

The last chapter is a refreshing approach to the relatively new technique of chronopotentiometry. The development is particularly well suited to student understanding and yet the non-mathematical treatment leaves nothing to be desired. While the reviewer would have preferred that Professor Lingane had drawn diagrams of chronopotentiograms with the axes in the opposite sense, a 90° crick in the neck is a small price indeed for the privilege of owning this book.

RALPH N. ADAMS
University of Kansas
Lawrence

The Study of the Physical World

Nicholas D. Cheronis, Brooklyn College; *James B. Parsons*, University of Chicago; *Conrad E. Ronneberg*, Denison University. 3rd ed. Houghton-Mifflin Co., Boston, Mass., 1958. vii + 684 pp. Many figs. and tables. 18.5 × 25 cm. $7.50.

The third edition of this college physical science text reduces the scope of coverage of earlier editions and has been rearranged to give greater unity. The treatment of topics is in general on a high plane and the college student will find a considerable amount of challenge here.

The materials on geology have been located together early in the text. This has the virtue of presenting fresh materials at the start (only few students have taken geology in high school) and of postponing until later, the introduction of mathematics, often the shoal upon which many a beginner is shipwrecked. The illustrations in the section on geology are particularly good, though they are in general of commendable quality throughout.

The attention given to electronic structure and chemical bonding is more extensive than in most texts of this type and in keeping with a modern trend in the teaching of chemistry. There are also three excellent chapters entitled Things of This World. One of these, the chapter on polymers, for example, goes much beyond just a reciting of their properties and discusses some of the most important relations between properties and molecular structure. The material on radioactivity and nuclear energy has been modernized and extended.

Each chapter closes with a summary, a well-selected and quite varied list of study exercises and suggested readings. A good sense of proportion has been maintained in treating the social aspects of science. The student is made aware of the fact that science is not a separate compartment of knowledge but an integral part of man's striving for a better world.

The inevitable errors which creep into any textbook have been kept to a minimum. On page 638, the statement, "The neutrons from a fission reaction . . . are too energetic to be captured by U^{235} nuclei and hence do not produce fission," would appear to preclude the possibility of an atomic bomb, which presumably depends on fast fission.

All in all, this is a well-written, interesting and attractive volume.

DONALD S. ALLEN
State University Teachers College
New Paltz, New York

Gmelins Handbuch der Anorganischen Chemie. System 45. Germanium Supplement.

Edited by the Gmelin Institute under the direction of *E. H. E. Pietsch*. 8th ed. Verlag Chemie, GmbH., Weinheim/Bergstr., 1958. xliv + 576 pp. 290 graphs. 17.5 × 25.5 cm. $80.88.

The growth in the importance of germanium in technology since the appearance of the original volume on germanium in 1931 is indicated by a comparison of their sizes (1931, 62 pp.; 1958, 576 pp.). The direction of the growth is shown by the fact that 414 pages of the present supplement are devoted to the physics of this element.

Despite this emphasis, the chemistry of germanium has been covered very adequately. In addition to preparation of the element and its compounds, a survey of compounds with carbon which are analogous to the silico-organic compounds is included. The analytical chemistry of germanium is treated in detail.

The literature coverage is through 1953 for most of the work and through 1954 for optical, electrical, and photoelectric properties.

The table of contents is given in both English and German which facilitates its use by American workers.

THOMAS E. FERINGTON
The College of Wooster
Wooster, Ohio

Low Temperature Physics and Chemistry

Edited by *John R. Dillinger*. University of Wisconsin Press, Madison, Wis., 1958. xxv + 676 pp. Many figs. and tables. 16.5 × 24.5 cm. $6.

This book is a summary of material presented at the Fifth International Conference on Low Temperature Physics and Chemistry held at the University of Wisconsin in August, 1957. The summary consists of some 225 contributions in the form of papers, approximately 1000 words in length, which include important tables and figures. The contributions represent work carried out in most major low temperature laboratories in the world excepting those of U.S.S.R.

For the convenience of the user, the papers have been arranged into 27 chapters according to subject. When the areas of research are broken down, it is found that about half of the papers deal with the two perennial favorites, superconductivity and the theory and physical properties of He^4, He^3 and their mixtures. Another quarter of the papers are concerned with magnetic properties of matter such as ferromagnetism, paramagnetism, susceptibilities, etc. Two important but not so popular areas, nuclear orientation experiments and temperature scale and measurements, are covered in about ten papers each. About 30 papers are devoted to the specific heat, electrical and thermal conductivity of elements, compounds, and alloys.

The book is lithoprinted with the result that a reduction of cost over usual print is achieved with some sacrifice in legibility. The graphs and figures in a number of cases are so poorly drawn or so reduced in size as to impair their value to the reader. Also, in some papers in which symbols or mathematical expressions printed by hand have been reproduced, reading is difficult.

The chief value of the book lies in the fact that here, in a group of concise papers containing all the important figures and tables, is a cross section of practically all the significant low temperature research in progress to the middle of the year 1957. It should prove extremely valuable in acting as a guide to the direction of future research in the low temperature field.

E. L. PACE
Western Reserve University
Cleveland, Ohio

Annual Review of Physical Chemistry. Volume 9

Edited by *H. Eyring*, University of Utah, *C. J. Christensen*, University of Utah, and *H. S. Johnston*, University of California. Annual Reviews, Inc., Palo Alto, Calif., 1958. vii + 511 pp. 16 × 23 cm. $7.

The present volume of the Annual Reviews covers the advances made in a number of important fields of physical chemistry. It surveys the literature which appeared in the year 1957 and it consists of 21 articles dealing respectively with thermochemistry, cryogenics, solutions of electrolytes, solutions of non-electrolytes, solid state, nuclear and electron-spin resonance, radiation chemistry, ion exchange resins and membranes, mechanical properties of high polymers, reaction kinetics and mechanisms of gas phase reactions, reaction kinetics in solution, quantum theory of electronic structure of molecules, surface chemistry and contact catalysis, physical organic chemistry, molecular electronic spectra, spectroscopy, experimental molecular structure, statistical mechanics, high pressure developments, optical rotatory power and colloid and surface chemistry.

It seems that the policy adopted by the editors consists in devoting the largest proportion of articles each year to the review of the same fields, while a small

number of articles is devoted to subjects deemed to require a more occasional treatment. Thus, the four topics mentioned last above replace topics appearing in the previous volume of the series (electrode processes, combustion and flames, proteins, and bond energies). It appears from the prospectus that they in turn will be replaced in volume 10 by reviews dealing with photosynthesis, stabilized free radicals, high temperature chemistry, and proteins and polypeptides. A more complete coverage is thus attempted.

Even with such policy, the rapid advance taking place in most fields, including new developments as well as the relationships between different topics, makes extensive coverage a difficult task. Reviewers have been left free to be predominantly guided by their main interests, and some have limited themselves to some aspect of their fields. To mention only two instances, the article on solutions of electrolytes pays particular attention to electrolytic conductance and the one on physical organic chemistry deals mostly with the effects of structure on reactivity.

The reviews are written by specialists, and mostly intended for specialists in the field or in closely related ones. They vary considerably from author to author in their critical approach, but all have maintained the high standards set by the previous volumes in the series. The reviewer has profited greatly from the reading of these articles dealing with topics in which he is particularly interested and believes that the present volume, like the previous ones, should be readily accessible to any worker in the field.

JOSE GOMEZ-IBANEZ
Wesleyan University
Middletown, Connecticut

Chemical Engineering Practice. Volume 4

Edited by *Herbert W. Cremer* and *Trefor Davis*. Academic Press, Inc., New York, 1958. vi + 623 + xix pp., Many figs. and tables. 16.5 × 25 cm. $17.50.

Volume 4 of "Chemical Engineering Practice" carries the subtitle "Fluid State," but the descriptive leaflet says it is devoted to Chemical Engineering Operations and Processes Involving Fluid Systems—Part I. Thinking in terms of unit operations it might be inferred that here was the book devoted to fluid flow. This would not be an illogical guess based on the descriptions of equipment and processes for crushing, grinding, and separation given in the preceding volume on the "Solid State."

Actually the first third of this volume is an excellent exposition of thermodynamics applied to physical systems. It has been prepared by Dr. Strickland-Constable of the University of London. He first reviews the first and second laws of thermodynamics, develops chemical potential as the criterion for equilibrium in a system, and derives general thermodynamic relationships. The next one hundred pages are used to discuss the thermodynamic properties of pure substances and mixtures. Formulas for work of compression and expansion are then derived (look out! F is the work function and G is the Gibbs function). This same chapter includes "sum and difference properties" and discusses the lever rule, triangular diagrams, liquid-liquid extraction, and distillation calculations. After this thorough and fundamental background, the basic equations of fluid flow are derived.

The group of chapters on fluid behavior are by Dr. Franklin of the A.E.A. and Mr. Cass of the University of Leeds. They deal in a more practical way with fluid statics, flow of viscous fluids, turbulence, flow in tubes and ducts, flow around objects, and flow of compressible fluids. Their treatment is more detailed and mathematical than the usual American texts on unit operations.

The final chapter (100 pages) on measurement of process variables is by Messrs. Pollard and Carruthers of the University of Leeds. This chapter is an elementary exposition on process instrumentation: the measurement of pressure, flow, and temperature.

The fine presentation of physical thermodynamics in this volume makes one anxious to see Volume 8, which is to contain the material on chemical thermodynamics. Fundamentals have been presented rigorously and well in this volume.

The only question that comes to mind is how well the man with the B.S. degree in science can apply these principles and equations to the situations he encounters unless he has an ample number of illustrated problems that show the way in which the equations are applied.

The next two volumes are also on the "fluid state" and promise to have much of importance to the chemical engineer. The series is gathering momentum as it moves along and future volumes will be anticipated.

KENNETH A. KOBE
The University of Texas
Austin

Outlines of Enzyme Chemistry

J. B. Neilands and *Paul K. Stumpf*, University of California, Berkeley. 2nd ed. John Wiley & Sons, Inc., New York, 1958. xii + 411 pp. Many figs. and tables. 16 × 23.5 cm. $0.00.

For this second edition, the authors have expanded the treatment of metal ion equilibria, the mechanism of enzyme action, proteolytic enzymes, and nucleotide derivatives into full chapters. All of the other chapters have been brought up to date by the inclusion of work published since the first edition (1955), and a few have been almost totally rewritten. The largest new section is a 22-page table of enzymes and some of their properties. The net result is a useful revision of a good book.

The authors have presupposed a knowledge of chemistry, biochemistry, and physiology on the part of the student. This makes the last section (Metabolic Patterns (24) difficult for those who have had only the standard chemistry courses. However, the first three sections (General Principles, Physical Chemistry, and Types of Coenzymes and Enzymes) should be understandable to senior majors without special preparation. The large number of references included in each chapter will help meet the need for a more complete treatment for advanced workers. They provide a good introduction to the literature dealing with most topics of enzyme chemistry.

DONALD A. TARR
The College of Wooster
Wooster, Ohio

Reports of the Fourth Soviet Conference on Electrochemistry

The Academy of Sciences of the U.S.S.R., Division of Chemical Science. Consultants Bureau, Inc., New York, 1958. 89 pp. 21.5 × 27 cm. $12.

This is the collection of abstracts of papers presented at this conference on electrochemistry.

The general topics covered are General Questions on Electrochemical Kinetics and the Reaction Mechanism of Electrochemical Reduction, The Mechanism of Electrode Processes in Melts, Diffusion Kinetics, The Mechanism of Oxidation Reactions, The Passivity of Metals and Chemisorbed Layers, The Electrodeposition of Metals, Chemical Sources of Current, Electrolysis in The Chemical Industry, and The Electrochemical Processes of Nonferrous Metallurgy. A total of 121 abstracts is included in these general topics.

The abstracts are similar to those published for use by chemists who attend our scientific meetings. The quality of the abstracts varies through the entire range of those that tell rather clearly what the results and conclusions are to those that simply tell what was done.

To the American chemist probably the most significant quality of this manuscript is the over-all perspective that the reader can gain concerning the breadth and quality of research done in Russia in this field. It appears to the reviewer to depict a good substantial program in electrochemistry.

A. B. GARRETT
Ohio State University
Columbus

Handbook of Chemical Microscopy. Volume 1

Émile Monnin Chamot and *Clyde Walter Mason*, Cornell University. 3rd ed. John Wiley & Sons, Inc., New York, 1958. xii + 502 pp. 15.5 × 23.5 cm. $14.

This timely third edition of the "Handbook of Chemical Microscopy" appears after a period of two decades during which time major advances have been made both in the tools and techniques of microscopy. While the book follows the general format of the previous edition, some major

changes have been made. A separate chapter has been devoted to the relationship of optical properties to crystal structure with expansion of the subject matter and inclusion of laboratory experiments. The chapter on refractive index determination has been moved to follow the chapter on the study of materials by means of the polarizing microscope which is a more logical sequence of presentation than appeared in previous editions. The chapter on the polarizing microscope has been expanded to include a discussion and illustrations of the ellipsoids of revolution for the wave fronts and refractive indices of uniaxial and biaxial materials which are essential for an understanding of the interference phenomena observed with conoscopic polarized light. Also included is a colored reproduction of the Michel-Levy chart for birefringence.

The chapter on ultramicroscopy has been revised and enlarged to conform to the modern understanding of colloidal phenomena with emphasis on the continuity of colloid chemistry with surface chemistry. Laboratory experiments are included to emphasize this point.

Extensive reference is made throughout the text to the application of the electron microscope to the solution of chemical problems. The separate new chapter on the electron microscope, while it will give the student an appreciation for this field, unfortunately overemphasizes both the difficulties encountered in the use of the electron microscope as well as the difficulties in the interpretation of the results, which may discourage the student from a more serious look at this important tool.

The author has excellently integrated all of the recent developments in both instrumentation and methodology into this well-established "Handbook of Chemical Microscopy." The book is well indexed and referenced for background reading and, as a result of the extensive revisions made, will be even more considered the Bible of the student of chemical microscopy than its predecessors.

CHARLES MARESH
American Cyanamid Company
Bound Brook, New Jersey

Synthetic Methods of Organic Chemistry. Volume 12

W. Theilheimer. Interscience Publishers, Inc., New York, 1958. xvi + 546 pp. 16.5 × 23.5 cm. $22.25.

The preface to preceding volumes states the purpose of this annual publication: "New methods for the synthesis of organic compounds, improvements of known methods, and also old proved methods scattered in periodicals, are being recorded continuously in this book series." The usage of reaction symbols is defended on the basis of systematic classification without reference to trivial and author names.

Volume 12 lists 965 abstracts of organic syntheses which appeared between 1955 and 1957. A survey of the total references (1549) showed that the origins of the abstracts paralleled those presented for Volume 7 (THIS JOURNAL, **32**, 222 (1955)). They are as follows: (the percentages from Volume 7, from a sample of 250 abstracts, are given in parentheses) 56% American (60); 17.5% British (17); 12.7% German (9); 3.9% Swiss (5); 3.6% Russian (2); 2.2% French (4); 1.3% Czech (0); 0.5% Scandinavian (2); and 2.0% others (1). The others are from Belgium, India, China, Japan, etc.

"Synthetic Methods of Organic Chemistry" represents a valuable systematic survey for the professional organic chemist. Outstanding features include an index with excellent cross-references, a systematic survey of reaction symbols for Volumes 11 and 12, together with supplementary references to Volumes 11 and 12 and a subdivision of reagents. Volume 12 also includes a review, Trends in Synthetic Organic Chemistry, 1958, which is of great value to the seasoned organic chemist.

ROY G. BOSSERT
Ohio Wesleyan University
Delaware

The Theory of the Properties of Metals and Alloys

N. F. Mott and *H. Jones.* Dover Publications, Inc., New York, 1959. xiii + 319 pp. 108 figs. 14.5 × 21.5 cm. Paper bound. $1.85.

Elasticity, Plasticity, and Structure of Matter

R. Houwink. Dover Publications, Inc., New York, 1959. xviii + 368 pp. 214 figs. 40 tables. 14 × 20.5 cm. Paper bound. $2.45.

These classic works have been reissued in paper back. Anyone presuming to have a modern view of the solid state knows how valuable these books are. Worn out copies can now be replaced and many copies can be added to personal libraries. Thanks, Dover!

W. F. K.

Conference on Extremely High Temperatures

Edited by *Heinz Fischer* and *Lawrence C. Mansur,* Air Force Cambridge Research Center. John Wiley & Sons, Inc., New York, 1958. xi + 258 pp. Many figs. and tables. 22.5 × 28.5 cm. $9.75.

This book is apparently taken verbatim from tape recordings of a conference held March 18 to 19, 1958, in Boston, Massachusetts, judging from such sentences as the opening one "Good morning, I am Dr. Hollingsworth." It therefore suffers from all of the deficiencies of such literal transcriptions.

On the other hand, the illustrations are well done and many in number, the speakers are the top authorities in their respective fields, and their remarks, though disjointed and hard for a non-expert in the field to comprehend, are authoritative.

The book is divided into four sections: (A) The Production of Extremely High Temperatures, (B) Methods of Temperature Measurement—Optical Radiation, (C) Plasma Analysis, (D) Applications. Five or six papers are included in each division.

J. A. CAMPBELL
Harvey Mudd College
Claremont, California

The Infrared Spectra of Complex Molecules

L. J. Bellamy, Senior Principal Officer, Ministry of Supply, London. 2nd ed. John Wiley & Sons, Inc., New York. 1958. 30 Figs. xvii + 425 pp. 15 × 22 cm. $8.

Only four years have elapsed since the first edition of this book. The present edition is about 100 pages longer than the first; this is due in part to a new chapter on the origin of group frequency shifts, and part to more information put in the older chapters. Out of some 250 sections discussing specific group frequency and intensity shifts, twenty are new. The brief correlation tables have, in spite of this, been scarcely affected. The 30 figures are identical with the first edition.

In bringing the literature up to date, the author states he has added over 700 new references. A breakdown of this increase shows the greatest activity in carbonyl correlations, followed by the chapter on amides, proteins, and polypeptides. Discussion of other nitrogen compounds has been significantly expanded.

Many people will find the new chapter the most valuable addition, though it will surely generate debate; others will find the recent literature addition most helpful. While the first edition is not obsolete, most of those who purchased it will need to have the second.

DAVID F. EGGERS, JR.
University of Washington
Seattle

An Introduction to the Chemistry of Fats and Fatty Acids

F. D. Gunstone, Lecturer in Chemistry, The University of St. Andrews. John Wiley & Sons, Inc., New York, 1958. x + 161 pp. 16 × 25 cm. $6.

In this brief but fairly comprehensive treatment of the basic aspects of the chemistry of naturally-occurring fats and fatty acids, the needs of advanced undergraduate and beginning graduate students have been kept primarily in mind. It is assumed that the reader has a fundamental working knowledge of organic chemistry, but most of the more specialized reactions

(Continued on page A418)